

Fuel and Lubricant Technologies

2016 Annual Report

Vehicle Technologies Office

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Acknowledgments

We would like to express our sincere appreciation to Alliance Technical Services, Inc. and Oak Ridge National Laboratory for their technical and artistic contributions in preparing and publishing this report.

In addition, we would like to thank all the participants for their contributions to the programs and all the authors who prepared the project abstracts that comprise this report.

Nomenclature

List of Acronyms, Abbreviations, and Definitions

1D	one-dimensional
3D	three-dimensional
AART	adjustable-angle reciprocating tribometer
ACI	advanced compression ignition
ADC	advanced distillation curve
AEC	Advanced Engine Combustion
AFIDA	advanced fuel ignition delay analyzer
Ag	silver
AHRR	apparent heat release rate
AI50	location of 50% mass fraction burned
AKI	anti-knock index; $(RON + MON)/2$
Al	aluminum
ANL	Argonne National Laboratory
Ar	argon
aSOI	after start of ignition
ATDC	after top dead center
atm	atmosphere
ATRP	atom transfer radical polymerization
ATS	aftertreatment system
ave	average
AVFL	Advanced Vehicle/Fuel/Lubricants
AW	antiwear
BDC	bottom dead center
BL	base lubricant
BL	boundary lubrication
BMEP	brake mean effective pressure
BOD	ball-on-disc
BPF	Berkeley Packet Filter
BRS	bio-reformate surrogate

BSFC	brake specific fuel consumption
BTE	brake thermal efficiency
C12	dodecanethiol
C18Cyc	cyclen with side chain length of C18
C18amine	amine with side chain length of C18
CA	crank angle
CA10	crank angle at which 10% of the heat has been released or mass fraction burned
CA50	crank angle at which 50% of the heat has been released or mass fraction burned
CAD	crank angle degrees
CCS	cold cranking simulator
CDC	conventional diesel combustion
CF	certification fuel
CFD	computational fluid dynamics
CF-E0	Tier 2 certification fuel
CFR	Cooperative Fuel Research
CH ₄	methane
CI	compression ignition
CL	chemiluminescence
CMOS	complementary metal-oxide semiconductor
CNG	compressed natural gas
CO	carbon monoxide
COF	coefficient of friction
Co-Optima	Co-Optimization of Fuels & Engines
COV	coefficient of variance
COV _{IMEP}	coefficient of variance in indicated mean effective pressure
cP	centipoise
CP	criteria pollutant
CPN	cyclopentanone
Cr	chromium
CR	common rail
CR	compression ratio

CRC	Coordinating Research Council
cSt	centistoke
Cu	copper
CVCC	constant volume combustion chamber
dATDC	degrees after top dead center
dB	decibel
DBE	double bond equivalent
D-cyl	dedicated cylinder
D-EGR [®]	Dedicated Exhaust Gas Recirculation
DFI	ducted fuel injection
DHA	detailed hydrocarbon analysis
DI	direct injection
DISI	direct injection spark ignition
DLC	diamond-like carbon
DLS	dynamic light scattering
DP	degree of polymerization
DSC	differential scanning calorimetry
DV	dynamic viscosity
E0	100% gasoline
E10	blend of 10% ethanol, 90% gasoline
E100	100% ethanol
E20	blend of 20% ethanol, 80% gasoline
E30	blend of 30% ethanol, 70% gasoline
E40	blend of 40% ethanol, 60% gasoline
E50	blend of 50% ethanol, 50% gasoline
E85	blend of 85% ethanol, 15% gasoline
E_A	activation energy
EDPCI	E85/Diesel Premixed Compression Ignition
EDS	energy-dispersive X-ray spectroscopy
EDTA	ethylenediaminetetraacetic acid
EGR	exhaust gas recirculation
EO	engine-out

EP	extreme pressure
etc.	<i>et cetera</i> (and so forth)
eV	electronvolt
FACE	Fuels for Advanced Combustion Engines
FBP	final boiling point
FE	fuel efficiency
FEI	fuel economy improvement
FM	friction modifier
FMC	Ford Motor Company
FOA	funding opportunity announcement
fps	feet per second
FREI	flames with repetitive extinction and ignition
FSN	Filter Smoke Number
FTP	Federal Test Procedure
FUL	full useful life
FWHM	full width at half maximum
FY	fiscal year
g	gram
g/bhph	grams per brake horsepower-hour
GCI	gasoline compression ignition
GC-MS	gas chromatograph–mass spectrometer
GDI	gasoline direct injection
GHG	greenhouse gas
GIMEP	gross indicated mean effective pressure
GITE	gross indicated thermal efficiency
g/kWh	grams per kilowatt-hour
GM	General Motors
GPa	gigapascal
GPF	gasoline particulate filter
G_{rel}	camera gain relative to that for proper natural luminosity image exposure
GTDI	gasoline turbocharged direct injection

GTL	gas-to-liquid
h	hour
H ₂	diatomic hydrogen
HC	hydrocarbon
HCCI	homogeneous charge compression ignition
HECO-SING	High-Efficiency Cost-Optimized Spark-Ignited Natural Gas
HFIR	High Flux Isotope Reactor
HFRR	High Frequency Reciprocating Rig
HFS	heavy fuel stratification
HHDD	heavy, heavy-duty diesel
HIE	high ignition energy
HNP-SiO ₂	hairy silica nanoparticles
HNP-SiO ₂	hairy titania nanoparticles
HoV, HOV	heat of vaporization
HR	heat release
HRR	heat release rate
HT	high tumble
HTHR	high temperature heat release
HTHS	high temperature high shear
HWFET	Highway Fuel Economy Test
Hz	hertz
IAT	intake air temperature
IBP	initial boiling point
iBu12	12% isobutanol in gasoline
ID	ignition delay
ID	inside diameter
i.e.	<i>id est</i> (that is)
IL	ionic liquid
IL-SiO ₂ NPs	ionic liquid modified silica nanoparticles
IMEP	indicated mean effective pressure
IQT	ignition quality tester
IR	infrared

ISNO _x	indicated specific NO _x
ISPM	indicated specific particulate matter
ITE	indicated thermal efficiency
J	joule
JSR	jet-stirred reactor
K	an empirical engine factor used in calculating octane index
K	kelvin
KI	knock integral
KI	knock intensity
KL-CA50	knock-limited combustion phasing
kPa	kilopascal
KV	kinematic viscosity
KV100	kinematic viscosity at 100°C
KV40	kinematic viscosity at 40°C
L	liter
lb	pound
lbf	pound-force
LFS	laminar flame speed
LHV	lower heating value
LIE	low ignition energy
LII	laser-induced incandescence
LLFC	leaner lifted-flame combustion
LLNL	Lawrence Livermore National Laboratory
LSPI	low speed pre-ignition
LT	low tumble
LTC	low temperature combustion
LTGC	low temperature gasoline combustion
LTHR	low temperature heat release
Mbbl/d	thousand barrels per day
MBMS	molecular beam mass spectrometer
MBT	maximum brake torque
MD	molecular dynamics

min	minute
mL	milliliter
mm	millimeter
mm/s	millimeters per second
$M_{n,SEC}$	number average molecular weight determined by size exclusion chromatography
Mo	molybdenum
MON	Motor Octane Number
MoS ₂	molybdenum disulfide
MOU	memorandum of understanding
MPa	megapascal
mpg	miles per gallon
mph	miles per hour
MRV	mini-rotary viscometer
MSS	AVL Micro-Soot Sensor
MTM	Mini Traction Machine
N	Newton
N	no
NA	no additive
NG	natural gas
NL	natural luminosity
nm	nanometer
N/M	not measured
NMEP	net mean effective pressure
NMHC	non-methane hydrocarbon
NMR	nuclear magnetic resonance
NO _x	oxides of nitrogen
NP	nanoparticle
NREL	National Renewable Energy Laboratory
ns	nanosecond
NTC	negative temperature coefficient
NU	Northwestern University

O ₂	diatomic oxygen
OCP	olefin copolymer
OH*	electronically excited hydroxyl radical
OI	Octane Index
ON	Octane Number
ORNL	Oak Ridge National Laboratory
OS	octane sensitivity
OSP	oil soluble polyalkylene glycol
P	phosphorus
[P ₆₆₆₁₄][C ₁₇ H ₃₅ COO]	phosphonium–carboxylate ionic liquid
[P ₆₆₆₁₄][RSO ₃]	phosphonium–sulfonate ionic liquid
[P ₈₈₈₈][DEHP]	phosphonium–phosphate ionic liquid
PAG	polyalkylene glycol
PAO	polyalphaolefin
PAO10	10 cSt polyalphaolefin
PAO-4	4 cSt polyalphaolefin
Pd	palladium
PDI	polydispersity index
PE	polyethylene
PFI	port fuel injection
P _{in}	intake air pressure
PM	particulate matter
PMI	Particulate Matter Index
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
PRF	Primary Reference Fuel
PSHR	pre-spark heat release
psig	pounds per square inch gage
PTWA	plasma transferred wire arc
PVD	physical vapor deposited
Ra	roughness average

RCCI	reactivity controlled compression ignition
RCM	rapid compression machine
RD5-87	fully blended research gasoline with 10% ethanol and an anti-knock index of 87
Reg-E0	regular grade gasoline containing zero ethanol
Reg-E10	regular grade gasoline containing 10% ethanol by volume
RI	Ringing Intensity
RMCSET	Ramped Modal Cycle Supplemental Emissions Test
ROHR	rate of heat release
RON	Research Octane Number
rpm	revolutions per minute
RT	room temperature
s	second
S	octane sensitivity
SANS	small-angle neutron scattering
SCR	selective catalyst reduction
SEM	scanning electron microscope
SET	Supplement Emissions Test
Si	silicon
SI	spark ignition
SINL	spatially integrated natural luminosity
SNL	Sandia National Laboratories
SOC	start of combustion
SOI	start of injection
SP+	bis(trioctyl(4-vinylbenzyl)phosphonium bis(2-ethylhexyl)phosphate
SPI	stochastic pre-ignition
SPIP _{ave}	average stochastic pre-ignition peak pressure
SPIP _{max}	maximum stochastic pre-ignition peak pressure
SSI	shear stability index
ST	spark timing
Std-PFS	standard partial fuel stratification
STLE	Society of Tribologists and Lubrication Engineers

SwRI	Southwest Research Institute [®]
T10	temperature at 10% conversion or 10% distilled
T50	blend of 50 vol% certification fuel with 50 vol% tri-propylene glycol methyl ether
T50	temperature at 50% conversion or 50% distilled
T90	temperature at 90% conversion or 90% distilled
TBBT	4-(tert-Butyl)benzyl thiol)
TDC	top dead center
TEM	transmission electron microscopy
TF	temperature of final boiling point
TGA	thermogravimetric analysis
THC	total hydrocarbon
T_{in}	intake temperature
TKE	turbulent kinetic energy
TOST	Thermal Oxidative Stability Testing
T-P	temperature–pressure
TP	tailpipe
TPRF	toluene primary reference fuel
TRF	toluene reference fuel
TSF	toluene standardization fuel
TWC	three-way catalyst
UDDS	Urban Dynamometer Driving Schedule
UI	upstream injection
ULSD	ultra-low sulfur diesel
UM	University of Michigan
US06	Supplementary Federal test Procedure
VI	viscosity index
VII	viscosity index improver
Vis.	visible
VM	viscosity modifier
VN	vanadium nitride
VP(443K)	vapor pressure at a temperature of 443 K

v/v	volume fraction
W	Watt
WBG	wood-derived biogasoline
WOT	wide open throttle
WP10NG	Weichai Power 10-L natural gas engine
wt%	weight percent
w/w	weight fraction
X_{O_2}	mole fraction of oxygen
Y	yes
ZDDP	zinc dialkyldithiophosphate
Zero-RK	Zero Order Reaction Kinetics, LLNL's high performance chemistry solver

List of Symbols

~	approximately
$^{\circ}\text{bTDC}$	degrees before top dead center
$^{\circ}\text{C}$	degrees Centigrade
$^{\circ}\text{CA}$	degrees crank angle
ΔP_{engine}	pressure ratio between intake pressure minus exhaust pressure
γ	ratio of specific heats
>	greater than
λ	excess air ratio
<	less than
μFIT	Microliter Fuel Ignition Tester
μL	microliter
$\mu\text{L}/\text{min}$	microliters per minute
μm	micrometer
μs	microsecond
%	percent
ϕ	fuel-air equivalence ratio
+	plus
#	number
τ_{RCM}	ignition delay time
ξ	correlation parameter

Executive Summary

On behalf of the Department of Energy's Vehicle Technologies Office, we are pleased to introduce the Fiscal Year 2016 Annual Progress Report for Fuel & Lubricant Technologies. The benefits of advanced fuel and lubricant technologies include:

- **Energy security:** Advanced fuels and lubricants enable more efficient engines that improve fuel economy. Enabling fuel diversification reduces the demand for imported petroleum and maximizes the use of domestic resources.
- **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, lower maintenance costs, superior in-use performance, and technologies which improve fuel economy. Innovations in fuels and lubricants reduce operating costs for consumers and businesses and help drive economic development and improve the global competitiveness of domestic industries.
- **Environmental sustainability:** Cleaner fuels have the potential to reduce engine-out emissions and enable efficient and durable emissions control technologies. Advanced lubricants are more environmentally friendly and reduce oil additive effects on the effectiveness and durability of emissions control equipment.

The objectives of the Fuel & Lubricant Technologies subprogram are: (1) to identify the critical fuel properties needed to enable advanced engine architectures and emission control systems that optimize engine efficiency and operability; (2) increase energy security by enabling direct fuel substitution of emerging domestic fuels; and (3) reduce parasitic losses in vehicles through the development of advanced lubrication technology.

In Fiscal Year 2016, the work on the Co-Optimization of Fuels and Engines program got underway at DOE national laboratories. This program, which is a collaboration with the Bioenergy Technology Office, has brought together nine national laboratories to collaborate on research aimed at identifying the fuel properties and engine design characteristics needed to maximize vehicle performance and affordability. The work seeks to maximize spark-ignited engine efficiency for the near-term light-duty market, while also exploring advanced compression-ignition concepts as a longer-term strategy for the heavy-duty market.

The Vehicle Technologies Office competitively awards funding through funding opportunity announcement selections and projects are fully funded through the duration of the project in the year the funding is awarded. Future work for direct funded projects at the national laboratories is subject to change based on annual appropriations. We are encouraged by the technical progress realized under this dynamic program in Fiscal Year 2016, and while we are conscious of the significant technical barriers, we see the research under this program provides a path to our goal – better fuels and better vehicles, sooner.

Kevin Stork
Technology Development Manager

Michael Weismiller
Technology Development Manager

Fuel & Lubricant Technologies
Vehicle Technologies Office

Table of Contents

Acknowledgments	i
Nomenclature	ii
Executive Summary.	xiii
I. Introduction	1
II. Co-Optimization of Fuels and Engines: Light-Duty	26
II.1 Alternative Fuels DISI Engine Research – Autoignition Metrics.	27
II.2 Studies of Research Octane Number (RON) and Heat of Vaporization (HoV)	33
II.3 Improving Vehicle Fuel Economy Through Increasing Fuel Octane Ratings	38
II.4 Alternative Fuels DISI Engine Research – Stratified Lean and Homogeneous Lean	41
II.5 Fuel Effects on EGR and Lean Dilution Limits on SI Combustion.	46
II.6 Co-Optima: Gasoline-Like Fuel Effects at High Load.	50
II.7 Extension of the Particulate Matter Index (PMI) for Gasoline Blended with Oxygenates.	55
II.8 GDI Fuel Effects on PM Emissions	61
II.9 Fuel Compatibility and Opportunities with Emissions Controls.	65
II.10 Heat of Vaporization Measurement and Engine Knock Limit Effects	70
III. Co-Optimization of Fuels and Engines: Medium/Heavy-Duty	77
III.1 Investigation on the Combustion of Selected High RON (Co-Optima) Fuels under GCI Operating Conditions	78
III.2 Autoignition Fundamentals of Fuels for Boosted SI and LTGC Engines	84
III.3 Accelerate Development of ACI/LTC: ORNL Single- and Dual-Fuel ACI	90
III.4 Accelerate Development of ACI/LTC: Fuel Effects on RCCI Combustion	95
III.5 Improved Mixing-Controlled Combustion Technologies and Fuels for High-Efficiency Compression Ignition Engines	100
III.6 Small-Volume Fuel Autoignition Tester Development	107

III.	Co-Optimization of Fuels and Engines: Medium/Heavy-Duty (Continued)	
III.7	Small Volume Autoignition Tester	113
III.8	The Microliter Fuel Ignition Tester (μ FIT): Creating a High Throughput Measurement Process for Small Sample Volumes	116
IV.	Co-Optimization of Fuels and Engines: Fuel Kinetics and Simulation.	121
IV.1	Fuel Property Database	122
IV.2	Fuel Property Blend Model	127
IV.3	Kinetic Mechanism Development	131
IV.4	Kinetic Mechanism Development and Validation	135
IV.5	Ignition Kinetics Experiments and Simulations to Support Advanced Engine Development	138
V.	Lubricants to Enable High Engine and Vehicle Fuel Efficiency.	143
V.1	Development of PAG (Polyalkylene Glycol)-Based Lubricant for Light- and Medium-Duty Axle Applications.	144
V.2	Power Cylinder Friction Reduction Through Coatings, Surface Finish, and Design	149
V.3	Hybrid Ionic-Nano-Additives for Engine Lubrication to Improve Fuel Efficiency	153
V.4	Integrated Friction Reduction Technology to Improve Fuel Economy without Sacrificing Durability	159
V.5	A Novel Lubricant Formulation Scheme for 2% Fuel Efficiency Improvement	166
V.6	Improve Fuel Economy Through Formulation Design and Modeling.	174
V.7	Lab-Engine Prediction and Correlation	179
V.8	Engine Friction Reduction Technologies	184
V.9	Phenomenological Modeling of Lubricant Film Formation and Performance	192
V.10	Characterizing Impact of Engine Lubricant and Fuel Properties on LSPI	197
V.11	Compatibility of Antiwear Additives with Non-Ferrous Engine Bearing Alloys	202
V.12	Lubricant Effects on Emissions and Emissions Control Devices	209
V.13	ORNL-GM: Development of Ionic Liquid-Additized, GF-5/6 Compatible Low-Viscosity Oils for Automotive Engine and Rear Axle Lubrication for 4% Improved Fuel Economy.	213

V. Lubricants to Enable High Engine and Vehicle Fuel Efficiency (Continued)

V.14 High Efficiency Lubricant Oils and Additives Research 218

V.15 Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and
Enhanced Lubricity of Engine Oils. 223

VI. Advanced Fuels & Engines 227

VI.1 Gasoline Engine and Fuels Offering Reduced Fuel Consumption and Emissions (GEFORCE). 228

VI.2 Unconventional and Renewable Hydrocarbon Fuels 231

VI.3 E85/Diesel Premixed Compression Ignition (EDPCI). 234

VI.4 Utilizing Alternative Fuel Ignition Properties to Improve SI and CI Engine Efficiency. 237

VI.5 Single-Fuel Reactivity Controlled Compression Ignition Combustion Enabled by Onboard
Fuel Reformation. 243

VI.6 Reduced Petroleum Use Through Easily-Reformed Fuels and Dedicated Exhaust Gas
Recirculation 247

VI.7 New Fuel Quality Metrics for GCI 249

VI.8 Efficiency-Optimized Dual-Fuel Engine with In-Cylinder Gasoline/CNG Blending 253

VI.9 High-Efficiency Cost-Optimized Spark-Ignited Natural Gas (HECO-SING) Engines. 259

VII. Index of Primary Contacts 266

VIII. Project Listings by Organizations 268

I. Introduction

I.1 Overview: Advancing Fuel and Lubricant Technology for an Efficient, Secure, and Clean Transportation System

Approach and Objectives

The Fuel & Lubricant Technologies subprogram supports fuels and lubricants research and development to provide vehicle manufacturers and users with cost-competitive options that enable higher fuel economy with low emissions, while also taking advantage of emerging domestic fuel sources. 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, and oils derived from plants, algae, and waste animal fats. This expectation brings new concerns for engine manufacturers, 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 high efficiency and high performance combustion strategies.

The Fuel & Lubricant Technologies subprogram activities are primarily focused on the properties and quality of finished fuel (as opposed to their production, which is part of the mission of the Bioenergy Technologies Office). The main thrust of the program is focused on the fuel properties that can enable innovative high-efficiency engine technologies. This approach is applied to light, medium, and heavy-duty vehicle applications. In parallel, we support analysis to understand the impacts of new fuels on energy usage, emissions, and economic growth. In addition, our subprogram activities also include research on the interaction of lubricants with new propulsion materials, fuels, aftertreatment devices, and other components, along with innovative solutions for reducing friction and wear. Lubrication fluids play an important role in reducing parasitic losses in the vehicle and enabling new technologies to be implemented while maintaining vehicle durability.

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 2007–2012 to enable the use of higher level ethanol blends in vehicles. This work was required to meet aggressive goals for renewable fuels established in the Energy Independence and Security Act (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 as part of this program. As of July 2017, over 900 stations in 29 states are offering E15. Beginning in 2012 General Motors (GM) began permitting (via statements in the owner’s manuals) the use of E15. In subsequent years, Ford, Toyota, Honda, Chrysler, and other manufacturers followed suit. As of model year 2017, the Renewable Fuels Association’s review of owner’s manuals indicates that some 80% of new vehicles are permitted by the manufacturer to use E15.

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 working group was initiated in 2013 and continues to work to evaluate the properties of new fuels for future, high-efficiency engines. The group’s plan for precompetitive research includes an emphasis on spark-ignition (SI) 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 (AKI) of fuels used in SI engines; and the determination of a new ignition delay metric for advanced low temperature combustion engines.

The Co-Optimization of Fuels and Engines (Co-Optima) initiative, which kicked-off in 2016, is a collaboration between the Advanced Engine and Fuels Technology program and the Bioenergy Technologies Office. The project formed a

national laboratory consortium to investigate the co-development of advanced fuels and engines for higher efficiency and lower emissions. Lifecycle and techno-economic analyses will guide the identification of new blendstock candidates that can be deployed rapidly, economically, and sustainably at the required scale of tens of billions of gallons per year. The targets of the Co-Optima initiative have become the primary goals of the Fuel & Lubricant Technologies subprogram:

- Improve passenger vehicle fuel economy by 50% by 2030, an additional 15% on top of continued engine development efforts. This would deliver an estimated \$30–\$40 billion in cost savings nationally.
- Increase energy independence with domestic biofuels by supplying as much as 15% of liquid fuels by 2035.

The new organization structure of the Vehicle Technologies Office has placed our subprogram within the newly created Advanced Engine and Fuels Technology program. This formalizes what was already a strong connection between engine and fuels research within the office. We will also continue working closely with the Bioenergy Technologies Office to understand the environmental and economic impacts of potential bio-based blendstocks for advanced fuels.

Co-Optimization of Fuels and Engines

Cars and light trucks accounted for 73% of the petroleum use in highway transportation in 2015. Gasoline (or petrol) accounts for 97% of the fuel used in these vehicles. In the quest for higher fuel economy, there has been a major trend during the last decade toward downsized, SI engines in light-duty vehicles. Downsized engines require higher power density than their larger predecessors, which is accomplished with boosted air handling systems and gasoline direct injection (GDI) fueling systems. In 2017, for instance, over 50% of new cars will use GDI and more than 20% will use turbochargers. However, the advance toward smaller engines is constrained by current fuel properties. Engine knock, caused by autoignition of the fuel before it can be consumed by the flame, limits the compression ratio and thus the efficiency of SI engines.

In the United States, gasoline grades are distinguished using the AKI, which is the average of the Research Octane Number and the Motor Octane Number. The vast majority of gasoline sold in the United States has an AKI of 87 (regular grade), with premium gasoline (AKI 90 or greater) accounting for 12% of sales. Although the average AKI of gasoline sold has been flat for roughly the last 40 years, the compression ratio of SI engines has increased significantly, enabled by advances in combustion chamber designs that decrease combustion duration and technologies such as knock sensors, electronic ignition systems, multiport fuel injection, and variable valve timing. However, further improvements in efficiency are limited by the existing fuel quality. Additionally, for the newest high-power-density engines which employ GDI and turbocharging, AKI has become an outdated metric and shows poor correlation with knock resistance.

Heavy-duty trucks and buses account for 27% of petroleum use in highway transportation. The fuel used in this class is overwhelmingly diesel (98%). Current heavy-duty diesel engines already have very high thermal efficiencies compared to SI engines, and the torque requirements required in this class are difficult to meet with SI engines. However, the aftertreatment systems needed to meet emissions standards with these engines are very expensive and require frequent maintenance. Furthermore, many projections of future fuel markets predict the demand for diesel will continue to grow sharply while the demand for gasoline will decline slightly. This could lead to a significant price disparity in the fuels or an oversupply of the lighter distillates from crude. Advanced compression ignition may present a solution to the dual issues of expensive aftertreatment and the changing demands for fuel.

The Co-Optima initiative is conducting the early-stage research needed to address the aforementioned barriers to more efficient light-duty and heavy-duty engines, as well as to accelerate the market introduction of advanced fuel and engine technologies. The research scope includes both SI and compression-ignition combustion approaches, targeting applications that impact the entire on-road fleet (light-, medium-, and heavy-duty vehicles). The initiative's major goals include significant improvements in vehicle fuel economy, lower-cost pathways to meet future emissions requirements, and a robust, diversified U.S. fuel resource base. The data, tools, and knowledge resulting from this program have the potential to enable advanced fuels that can significantly reduce transportation costs for consumers and businesses and help drive the global competitiveness of domestic industries. Blendstocks sourced from cellulosic biomass and similar non-food renewable and waste resources have the additional potential benefits of increasing U.S.-based jobs, supporting rural economies, reducing stresses on the environment, enhancing energy security, and expanding U.S. science and engineering leadership.

Co-Optima's coordinated engine and fuels research, coupled with detailed analysis, is providing the framework for the co-development of fuel and engine technologies that, when used in tandem, offer the greatest combination of efficiency, performance, and fuel diversification. Co-Optima's fuels research is focused on identifying fuel properties that enable optimized engine performance. This property-based approach is providing the technical information required to define future fuel requirements that are composition-agnostic, allowing the market to define the best means to blend and provide these fuels.

Energy Security and Emerging Domestic Fuels

In 2015, 92% of transportation energy in the U.S. came from petroleum. 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. 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. Oil sands account for more than half of the oil production in Canada, and the vast majority of their proven oil reserves. Since Canada is our largest supplier of crude oil, 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. Because it is a co-product of natural gas production, there has also been an increase in domestic propane production in the last five years, and propane continues to be a fuel of interest for fleets of buses and medium-duty vehicles. In 2016, the Fuel & Lubricant Technologies subprogram continued to advance gaseous fuels research to make better use of our national resources through a Funding Opportunity Announcement designed to remove barriers to the deployment of new, more efficient, direct injection propane engines. Ongoing research continues to improve the efficiency and emissions for natural gas engines. While much of the existing fundamental fuels combustion research will benefit gaseous fuels as well, future program activities will continue to target new gaseous fuel technologies that require early-stage, pre-competitive research to become viable.

The Energy Independence and Security Act of 2007 mandates increasing production of biofuel for use in transportation vehicles. In terms of starch-based ethanol, the United States is at the 15 billion gallon per year limit imposed by EISA, but has not met the EISA goals for advanced biofuels. The Fuel & Lubricant Technologies subprogram supports this energy independence goal through the Co-Optima initiative. The research under Co-Optima will help to accelerate the introduction of affordable, scalable, and sustainable fuels and high-efficiency, low-emission engines designed to work together in delivering maximum energy savings, emissions reduction, and on-road vehicle performance.

Biodiesel is a popular domestic and renewable fuel that supplements the supply of 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 in the early 2000s with biodiesel resulted in fuel filter clogging problems and cold weather operating problems in many trucks. As a result of this and similar problems with the quality of U.S. biodiesel, the Fuel & Lubricant Technologies subprogram partnered with the National Biodiesel Board to improve ASTM (an international standards organization) biodiesel fuel specifications and ensure that suppliers adhere to the specifications. Surveys of marketed biodiesel conducted by the Fuel & Lubricant Technologies subprogram showed a large improvement in compliance with the ASTM standard over the period of 2005–2012, including more consistent biodiesel concentration and reduced levels of impurities. The fuel quality improvement resulted in increased willingness among engine manufacturers to allow biodiesel use in their engines.

Reducing friction losses in engines and drivelines can significantly reduce fuel consumption across the entire vehicle fleet, reducing the cost of transportation and conserving energy. 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 laboratories, and industry to study many aspects of lubrication, from fundamental tribology to application of fully formulated lubricants in vehicles and engines.

Environmental Impacts of Advanced Fuels

The combustion process used to convert the energy in 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, which include carbon monoxide, oxides of nitrogen, particulate matter, volatile organic compounds, and sulfur dioxide, are currently controlled to very low levels by catalytic converters and other emissions control strategies. The Fuel & Lubricant Technologies subprogram is evaluating advanced petroleum and non-petroleum-based fuels for any potential impacts on engine-out emissions and emission control system efficiency and durability. Combustion of petroleum fuels also releases greenhouse gases (GHGs) that are believed to contribute to climate change. Advanced petroleum-based fuels can reduce GHGs through enabling more efficient engines, resulting in less fuel used per unit of work performed. In addition to being domestically sourced, renewable fuels that consume CO₂ from the atmosphere through the growth of their feedstock can reduce the lifecycle GHGs of transportation. In addition, detailed research has also demonstrated that black carbon emissions, which behave as potent GHGs, can be reduced by using biofuel blends in gasoline direct injection engines.

Conclusion

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. The remainder of this report highlights the progress achieved during the 2016 fiscal year. The following chapters will provide objectives, accomplishments, and technical details of the individual projects in the Fuel & Lubricant Technologies portfolio.

I.2 Summary of Program Accomplishments (FY 2016) and Future Activities (FY 2017)

The following presents highlights of the Fuel & Lubricant Technologies project accomplishments in Fiscal Year (FY) 2016 and the activities that will be pursued in FY 2017.

Co-Optimization of Fuels and Engines: Light-Duty

Projects in this research area consider advanced fuels to improve the efficiency and emissions of downsized, boosted, spark-ignited engines. Additional research focuses on defining fuel metrics that better represent performance of the fuel in these engines.

- **Sandia National Laboratories** are providing the science base needed by industry stakeholders to understand how engine design and operation can be co-optimized with future fuels for highest overall system efficiency. (**Sjöberg, report II.1**)

FY 2016 accomplishments: (1) finished a study on the use of partial fuel stratification to stabilize ultra-lean mixed-mode spark ignition (SI) combustion for gasoline and E85 (85% ethanol, 15% gasoline blend by volume) fuels over wide load ranges; (2) finished a study on the combined effects of intake flow and spark plug location on flame development, combustion stability and end-gas autoignition for lean SI engine operation using E30 (30% ethanol, 70% gasoline blend by volume) fuel; demonstrated the feasibility to apply optical diagnostics of the transition from deflagration to autoignition; (3) developed modeling methodology and provided validation data for an extensive chemical kinetics modeling study on the fuel-based origin of octane sensitivity; and (4) determined steady-state knock-limited combustion phasing over ranges of intake pressure and temperature for stoichiometric operation with a compression ratio of 12 using three Co-Optima Core Fuels with Research Octane Number = 98 and dissimilar composition.

FY 2017 activities: (1) expand stoichiometric knock study to higher intake pressures by reducing compression ratio to 10; (2) incorporate transient knock testing to increase real-world relevance of results; (3) incorporate new fuel components and blends in coordination with other Co-Optima teams; (4) optically measure turbulent deflagration rates for key fuel blends and compare results with existing database for laminar flame speed; and (5) continue examination of well-mixed lean or dilute SI operation while quantifying the relevance of Research Octane Number and Motor Octane Number for fuel reactivity under ultra-lean conditions.

- **Argonne National Laboratory** is investigating the effects of fuel properties on the characteristics of mixture auto-ignition using a well-instrumented Cooperative Fuel Research (CFR) F1/F2 fuel octane rating single-cylinder research engine. They will quantify the impact of fuel heat of vaporization (HoV) on measured Research Octane Number (RON) and develop a strategy to decouple HoV from measured RON. (**Kolodziej, report II.2**)

FY 2016 accomplishments: (1) installed, instrumented, and commissioned a CFR F1/F2 fuel octane research engine (Figure 1); (2) created one-dimensional GT-POWER model of CFR F1/F2 engine to calculate cylinder pressure and temperature conditions; (3) developed a matrix of primary reference fuel (PRF)–ethanol fuels to yield matched RON 98 for ethanol blends up to 50%; (4) characterized differences in lambda at peak knocking condition between standard PRF fuels and PRF–ethanol blends, with peak knocking occurring at 0.9 lambda for PRF fuels and 0.95 lambda for PRF–ethanol blends; and (5) established that the HoV effect of 50% ethanol exceeds 1 RON unit.

FY 2017 activities: (1) validate one-dimensional GT-POWER engine model to determine how fuel HoV affects cylinder pressure and temperature during RON measurement; (2) quantify the effect of ethanol HoV in full boiling range gasolines and expand on



Figure 1. Instrumented and commissioned CFR F1/F2 fuels rating test engine installed at Argonne National Laboratory (Kolodziej, report II.2)

PRF–ethanol results; and (3) decouple the HoV effect from RON for additional fuel hydrocarbons from the down-selected Co-Optimization of Fuels & Engine list of 20.

- **Oak Ridge National Laboratory** is quantifying 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. **(Sluder, report II.3)**

FY 2016 accomplishments: (1) procured fuels for U.S. DRIVE Fuels Working Group’s Fuel Set B; (2) completed engine studies of 97 Research Octane Number (RON) fuels in Fuel Set B; (3) began studies of 101 RON fuels in Fuel Set B; and (4) led development and procurement of the Co-Optima “core” fuels matrix of 97 RON fuels.

FY 2017 activities: (1) complete engine studies and vehicle modeling in support of the U.S. DRIVE Fuels Working Group’s well-to-wheels study; and (2) evaluate candidate fuel blends generated by the Co-Optima project for potential efficiency improvement in the Ford 1.6-L engine and in vehicle models.

- **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 being developed by industry, and how engine design and operation can be optimized for most efficient use of future fuels. **(Sjöberg, report II.4)**

FY 2016 accomplishments: (1) continued examination of effects of fuel blends on stratified operation at various speeds and intake pressures; (2) demonstrated infrared detection of vapor penetration of E85 (85% ethanol, 15% gasoline blend by volume) and gasoline fuel sprays; (3) investigated three Co-Optima Core Fuels for boosted stratified charge operation at 2,000 rpm; (4) used optical techniques to refine partial fuel stratification technique to allow the use of a smaller pilot fuel quantity while maintaining stable ultra-lean spark ignition combustion with an E30 (30% ethanol, 70% gasoline blend by volume) fuel; (5) used particle image velocimetry to measure effects of flow field on early flame development for well-mixed ultra-lean spark ignition operation with E30; and (6) packaged particle image velocimetry, flow and boundary conditions data, including a GT-POWER model, and transferred to computational fluid dynamics modelers at Argonne National Laboratory.

FY 2017 activities: (1) continue to further the scientific understanding of advanced and efficient combustion modes, using blends of gasoline, ethanol, and new biofuels in an optical direct-injected spark ignition engine; (2) incorporate new fuel components and blends in coordination with other Co-Optima tasks; (3) expand conceptual model of swirl–spray stabilization mechanism to include double injections of E0–E30 fuels for boosted stratified operation; (4) examine how the dominant soot production pathway of stratified charge combustion changes with operating conditions and fuel composition; (5) investigate experimentally lean or dilute well-mixed mixed-mode spark ignition combustion, with a focus on combustion stability and peak apparent heat release rate; and (6) support computational fluid dynamics and chemical kinetics modeling groups by providing validation data for in-cylinder flows, deflagration, and end-gas autoignition.

- **Argonne National Laboratory** is verifying the Co-Optimization of Fuels & Engines “Central Fuel Hypothesis” assumption that fuel laminar flame speed (LFS) can describe the limits of exhaust gas recirculation (EGR) and lean dilute spark ignition combustion. **(Kolodziej, report II.5)**

FY 2016 accomplishments: (1) determined that among alcohol blended fuels, increased fuel LFS and heat of vaporization (HoV) allowed for 4–6% increased EGR dilution and some lean tolerance increase (0.05–0.1 higher lambda), providing approximately 1–2% higher engine indicated thermal efficiency (ITE); (2) quantified that increased cylinder charge motion, either by tumble or direct injection, increased EGR dilution tolerance by 2% and lean limits by 0.1 lambda, providing approximately 1% higher engine ITE; (3) demonstrated that fuel LFS and HoV can have as big of an effect, if not larger, on engine EGR dilution limits and increased ITE than only changes to engine design parameters; and (4) ascertained that under lean conditions, engine design parameters that affect cylinder charge motion had a much larger effect on lean operating limits compared to fuel LFS and HoV changes.

FY 2017 activities: (1) expand experiments on the positive effects of fuel LFS and HoV for alcohol fuel blends, by comparing with other families of hydrocarbons; (2) combine chemical kinetic modeling with experiments to estimate combustion flame speeds at engine relevant conditions; and (3) test fuels from the Co-Optima down-selected list of 20 components of interest.

- **Oak Ridge National Laboratory** is investigating the validity of the Co-Optima central fuel hypothesis, which states that a fuel candidate should perform in a manner commensurate with its properties regardless of its chemistry. Specifically, this project is investigating the knock propensity of fuels under boosted operating conditions for stoichiometric spark-ignited (SI) engines. **(Szybist, report II.6)**

FY 2016 accomplishments: (1) identified the occurrence of pre-spark heat release (PSHR) in a stoichiometric SI engine, and its dependence on fuel composition; (2) successfully modeled the PSHR phenomenon using detailed chemical kinetics, for three different fuels, verifying that PSHR tendency decreases as octane sensitivity increases; and (3) identified that PSHR leads to a flame speed decrease for the main combustion event.

FY 2017 activities: (1) evaluate up to eight fuels in FY 2017 under boosted conditions in a stoichiometric engine, including the Co-Optima core fuel matrix and three Co-Optima biofuel candidates; (2) investigate the effect of exhaust gas recirculation on PSHR in a boosted SI engine with realistic air handling boundary conditions; and (3) analyze the experimental results using chemical kinetic simulations with bio-fuel mechanisms from Lawrence Livermore National Laboratory.

- **National Renewable Energy Laboratory** is characterizing qualitatively and quantitatively how oxygenated blending components affect the efficacy of the particulate matter index (PMI), a model which has demonstrated high accuracy in predicting particulate matter (PM) emissions from petroleum-based gasoline. **(Ratcliff, report II.7)**

FY 2016 accomplishments: (1) a full factorial experimental design of fuel composition was conceived to test the null hypothesis that gasolines having high heat of vaporization (HOV; in this case from adding ethanol) and low vapor pressure aromatics do not increase PM emissions; (2) the fuels were blended and analyzed by a gas chromatography method providing detailed hydrocarbon analysis, and from this the PMIs and HOVs of the fuels were computed (Figure 2); (3) the advanced distillation curve method was then used to characterize the changes in evaporated fuel composition as a function of percent fuel distilled; a new finding from the advanced distillation curve characterization was that ethanol blending delayed the evaporation of aromatics in the fuel to the end of the distillation process; (4) five of the fuels comprising a partial factorial design (one face of the full factorial design) were then combusted in a single-cylinder, gasoline direct injection engine and the PM emissions were measured at six distinct operating conditions; and (5) preliminary data analysis indicates that gasoline having both high HOV and low vapor pressure aromatics fueling a gasoline direct injection engine at 2,500 rpm produces higher PM emissions than predicted by the fuel's PMI; thus, it appears that the null hypothesis must be rejected for some cases investigated and therefore development of an improved PMI model seems warranted.

FY 2017 activities: (1) perform comprehensive data analysis from PM emissions measurements and obtain additional emissions data from other concentrations of the aromatic hydrocarbons per the full factorial design; (2) obtain PM emission data from one or two blends using an iso-paraffin with the same vapor pressure as one aromatic in the experimental design; these blends will serve as control fuels for comparison with aromatic blend results; (3) investigate oxygenate chemistry effects on PM emissions using oxygenates having the same vapor pressures and double bond equivalents as the single-ring alkyl aromatics in the present study; and (4) investigate alternate formulations of PMI to more accurately predict a blend component's propensity to form soot.

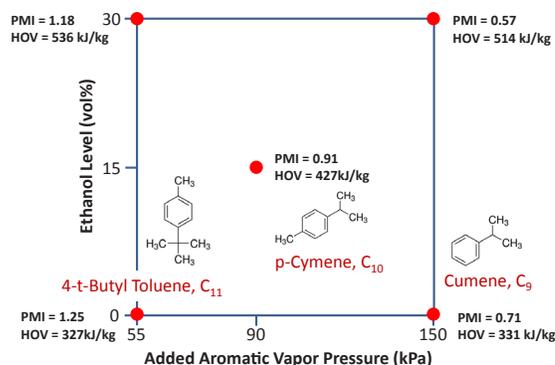


Figure 2. Partial factorial experimental design for fuel blends. Tested blends are indicated by red dots, with associated PMI and HOV values from detailed hydrocarbon analyses. Aromatic hydrocarbon vapor pressures on the X-axis are at 443 K (Ratcliff, report II.7)

- **Oak Ridge National Laboratory** is investigating the validity of the Co-Optima central fuel hypothesis, which states that a fuel candidate should perform in a manner commensurate with its properties regardless of its chemistry. Specifically, this project is investigating the impacts of candidate biofuel blends on the generation and composition of particulate matter (PM) emissions from gasoline direct injection (GDI) engines and assessing the potential for mitigation of GDI PM with emissions controls. **(Storey, report II.8)**

FY 2016 accomplishments: (1) evaluated soot oxidation kinetics for PM collected from a GDI engine operating on both 100% gasoline (E0) and a 30% ethanol–gasoline blend (E30); (2) demonstrated that GDI PM becomes more difficult to oxidize as regeneration progresses, unlike diesel PM which has a near constant activation energy; and (3) determined the soot layer thickness inside the gasoline particulate filter using neutron imaging.

FY 2017 activities: (1) continue neutron imaging studies of soot layer thickness, and (2) characterize PM emissions from a GDI engine operating on three candidate gasoline biofuel blends.

- **Oak Ridge National Laboratory** is investigating the compatibility of Co-Optima fuel candidates with emissions control systems and to identify opportunities for alternative emissions control strategies based on novel fuel chemistry. **(Toops, report II.9)**

FY 2016 accomplishments: (1) completed study on an automated synthetic exhaust flow reactor evaluating the benefits of a dual selective catalytic reduction emissions control strategy for controlling NO_x from a lean burn engine running on oxygenated biofuels; (2) published manuscripts in *Applied Catalysis B: Environmental and Catalysis Today* on alcohol–gasoline blends with a range of silver alumina catalysts; and (3) reported primary findings on the impact of trace metals in biodiesel in heavy-duty emissions control systems; presentations given at the 2015 Biodiesel Technical workshop, 10th International Congress on Catalysis and Automotive Pollution Control (CAPoC10), 9th International Conference on Environmental Catalysis, and SAE 2016 International Powertrains, Fuels & Lubricants Meeting; findings were reported in SAE International Journal of Fuels and Lubricants. A book chapter summarizing all of our recent efforts on this subject was also prepared and submitted to Royal Society of Chemistry, Thomas Graham House, Cambridge, UK (*Specialist Periodical Report (SPR) on Catalysis Volume 29*).

FY 2017 activities: (1) evaluate light-off temperature reactivity for new Co-Optima fuel candidates and the impact on total hydrocarbon emissions during cold start operation; (2) identify emissions control opportunities afforded by Co-Optima fuel candidates; and (3) identify potential impurities in primary Co-Optima fuel component candidates.

- **National Renewable Energy Laboratory** is clarifying the roles and interactions of octane sensitivity (S) and heat of vaporization (HOV) on the knock resistance of high-octane fuels in spark ignition engines, including development of improved methods for measurement of HOV. **(Fioroni, report II.10)**

FY 2016 accomplishments: (1) the differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) method was improved to obtain $\pm 2\%$ accuracy for most pure component materials. For highly volatile materials such as hexane, we were not able to obtain better than $\pm 3\%$ (an improvement over the initial $>10\%$ error observed); (2) a DSC method was developed in which greater accuracy was achieved relative to the DSC/TGA method. This is because of the higher sensitivity heat flow measurement in the DSC. We observed highly accurate results for many pure components, but again had issues with highly volatile compounds (Table 1). Additional improvements will be the focus of work in fiscal year 2017; and (3) research on fuel knock resistance in a single-cylinder gasoline direct-injection engine revealed a clear effect of HOV on performance. At retarded combustion phasing and intake air temperatures above 60°C, fuels with higher HOV enabled operation at significantly higher loads, i.e., showed improved knock resistance. This suggests that high-HOV fuels may improve fuel efficiency over real-world vehicle operating cycles by reducing the need for spark retard, fuel enrichment, and/or downshifting.

FY 2017 activities: (1) gain detailed information on how chemical composition affects instantaneous HOV, we will couple the DSC/TGA instrument to a high-resolution mass spectrometer. This will allow us to not only look at the heat evolved over time (partial HOV), but also to correlate the heat evolved with the species that are being evaporated at any given time in the evaporation curve; (2) further improve the DSC method to achieve better accuracy of pure components, especially those with high volatility. We also plan to extend the method to full boiling range gasoline

samples and blends with various oxygenates; and (3) additional engine experiments at 90°C intake air temperature with isooctane and the E25 fuel are required to complete the full analysis of these findings. In addition, we plan to extend the study with fuels having higher S (≈ 15) and lower S (≈ 6) than the present range of 11–12.

Co-Optimization of Fuels and Engines: Medium/Heavy-Duty

Projects in this research area consider fuels for advance engines primarily aimed at the medium- and heavy-duty sectors. The work in this area is focused on advanced compression ignition engines, including those employing kinetically controlled combustion, and the fuel properties needed to expand the operating range of these advance combustion strategies.

- **Argonne National Laboratory** is demonstrating adapted engine operation (1.9-L General Motors) on high octane fuels (aromatic, alkylate, E30 [30% ethanol, 70% gasoline blend]) for Co-Optima using an advanced combustion concept, gasoline compression ignition (GCI). (**Ciatti, report III.1**)

FY 2016 accomplishments: (1) developed GCI engine operating strategy to achieve a stable (coefficient of variation in indicated mean effective pressure < 3%), relatively low noise (~ 85 dB), low emission (hydrocarbon, CO < 5 g/kW-hr) and soot (<0.1) for all high Research Octane Number fuels at intermediate load (3–6 bar brake mean effective pressure); (2) quantified dilution limit (utilize low pressure exhaust gas recirculation [EGR] with maximum 30% EGR for stable combustion) for different global equivalence ratio conditions (1.6–2.0) at a given engine operating condition (constant combustion phasing $\sim 5^\circ$ after top dead center); (3) investigated the sensitivity on combustion phasing as boost and temperature are changed simultaneously and the corresponding effect on autoignition (assessment of low temperature heat release, intermediate temperature heat release); and (4) captured endoscope images to visualize the spray/combustion for various conditions: flame development of first and second injections; soot radiation comparison for different fuels (E30 showed lowest soot volume fraction levels).

FY 2017 activities: (1) continue exploring different engine speed and load (higher) that can be achieved with desirable engine outputs (soot, emission, noise, efficiency) under low temperature combustion condition; (2) provide engine conditions and data (cylinder pressure, emission, endoscope images) for computational fluid dynamics modeling to have simulations that can provide more insights on in-cylinder combustion process; (3) Correlate with Coordinating Fuel Research data to characterize the effect of heat of evaporation of the fuels on auto-ignition and noise; (4) investigate the correlation of pressure–temperature sensitivity, and fuel stratification between advanced compression ignition engine and rapid compression machine data to better understand the autoignition behavior of different high Research Octane Number fuels; and (5) obtain general characteristics of particulate matter through transmission electron microscope sampling for these fuels with very different aromatic content or particulate matter index under compression ignition condition.

- **Sandia National Laboratories** are providing a fundamental understanding of the autoignition behavior of advanced fuels at operating conditions relevant to boosted spark ignition and advanced compression ignition (ACI) engines. (**Dec, report III.2**)

FY 2016 accomplishments: (1) established initial fuels test matrix in collaboration with Oak Ridge Nation Laboratory, consisting of three Research Octane Number (RON) 98 fuels, one each with low sensitivity, high-sensitivity with 30% ethanol, and high-sensitivity with high aromatic content; (2) initiated an expansion of the fuels matrix to include two additional RON 98, high-sensitivity fuels with high-olefin and high-cycloalkane content; (3) established an engine operation test matrix for evaluating fuel effects for low temperature gasoline combustion (LTGC), performance related

Table 1. Measurement of HOV of Pure Compounds by DSC/TGA Using Improved Method (Fioroni, report II.10)

Compound	Literature Value	Measured Value	% Error	Vapor Pressure at 20°C (kPa)
Toluene	413	408	1.2	2.3
Ethanol	924	928	0.4	5.95
Isooctane	308	307	0.3	5.10
Hexane	366	384	4.9	17.6
Hexane*	366	375	2.7	17.6
2-Methylpentane	347	362	4.3	22.0

*Measured using a pan lid without laser-drilled hole.

to knock in SI engines, and to provide data for chemical–kinetic model validation; (4) acquired detailed LTGC engine performance data for the RON 98, high-aromatic fuel over the engine operation test matrix; (5) acquired similar detailed LTGC performance data for a regular grade E10 gasoline and compared results with the high-aromatic fuel to quantify differences; and (6) analyzed these new data and performed an initial assessment of the ability of the Octane Index to correlate the data from these fuels at naturally aspirated conditions.

FY 2017 activities: (1) acquire detailed LTGC engine performance data for the other fuels in the fuels test matrix, fuels with low-sensitivity, high-sensitivity with 30% ethanol, high-sensitivity with high-olefin content, and high-sensitivity with high-cycloalkane content; (2) analyze data for these four additional fuels and compare performance with that of the two fuel tested in FY 2016; (3) acquire LTGC performance data for other gasoline-like fuels that have high levels of bio-derived components; (4) evaluate these gasoline-like fuels for their potential to work in LTGC engines, including their ϕ -sensitivity; (5) work with the High Performance Fuels team to identify bio-fuel components with good potential for blending ACI fuels, and test the performance of these ACI fuels; and (6) provide data to the Toolkit team for chemical–kinetic model development and evaluation.

- **Oak Ridge National Laboratory** is investigating the validity of the Co-Optima central fuel hypothesis, which states that a fuel candidate should perform in a manner commensurate with its properties regardless of its chemistry. Specifically, this project is investigating the potential of the co-evolution of fuels and a subset of combustion strategies: single- and dual-fuel advanced compression ignition (ACI). (**Curran, report III.3**)

FY 2016 accomplishments: (1) demonstrated transient ACI via hardware-in-the-loop experiments and boosted, spark-ignition fuels; (2) collaboration with Sandia National Laboratories linking optical and metal experimental ACI results established; and (3) published gasoline compression ignition perspective paper linking ACI modes across of spectrum of stratification.

FY 2017 activities: (1) complete coordinated experiments with Sandia National Laboratories with selected fuel combinations for high- and low-delta dual-fuel ACI modes; (2) complete experimental campaign and data processing to assess fuel effects on emissions and efficiency for ACI combustion modes in support of merit function development; (3) investigate potential of ACI modes with electrified powertrains; and (4) transient experiments for research into fuel effects on ACI modes.

- **Sandia National Laboratories** are measuring in-cylinder mixing and kinetics to optimize dual-fuel heat release for noise, efficiency, and load range, and understanding mixing–ignition interaction for different fuel reactivity combinations. (**Musculus, report III.4**)

FY 2016 accomplishments: (1) characteristic features and trends in the apparent heat release rate (AHRR) for injection timing sweeps in the optical engine mirror those observed for the metal engine. Although key AHRR features occur at different timings in the two facilities, the characteristic behavior is the same, such that comparisons of data from the two experiments at operating conditions with similar AHRR features can provide insight into how in-cylinder processes observed in the optical engine affect engine performance and emissions observed in the all-metal engine; and (2) imaging data confirm expectations based on ignition delay trends that premixing controls the peak AHRR, and hence play a role in the load limits of reactivity controlled compression ignition (RCCI). Infrared emission imaging also reveals that inhomogeneities in the more well-mixed gasoline direct injection charge may also play a role in the AHRR characteristics (Figure 3).

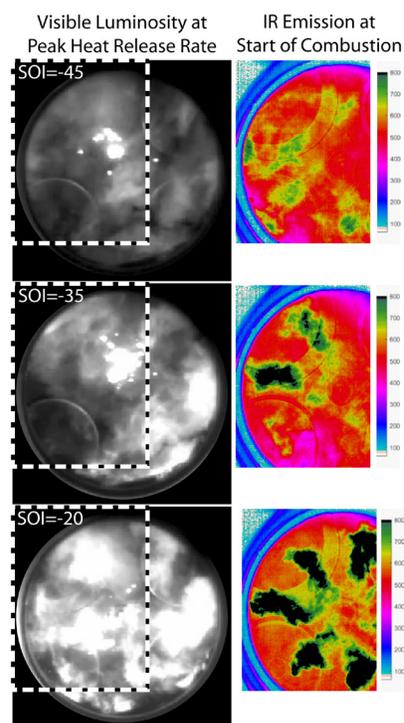


Figure 3. Images of natural combustion luminosity at the peak apparent heat release rate (left) and infrared (IR) emission at start of combustion (right) at three selected compression ratio start of injection (SOI) timings. The field of view for the visible luminosity images covers the entire piston bowl, while the IR camera field of view spans a portion of the bowl indicated by the dashed rectangles overlaid on the visible images. (Musculus, report III.4)

FY 2017 activities: (1) building on knowledge gained from FY 2016 experiments at Oak Ridge National Laboratory and Sandia National Laboratories, develop a joint experimental design to provide the most meaningful comparisons of data acquired from the two engine facilities; (2) apply quantitative mixing diagnostics to understand how engine hardware and operating conditions can be designed to help overcome operating condition range limits of RCCI for baseline test fuels; and (3) apply optical diagnostics using fuels with varying properties to understand how fuel properties couple with engine hardware and operating conditions at the operating condition range limits of RCCI.

- **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 III.5)**

FY 2016 accomplishments: (1) provided the first conclusive experiments showing that leaner lifted-flame combustion (LLFC) can be sustained in an engine to ~20% load using a realistic fuel injector configuration (i.e., a six-hole tip), practical operating conditions, and a feasible fuel. Fuel oxygenation was required, and one or more additional mixing enhancement strategies will be necessary to sustain LLFC at higher loads; (2) completed the analysis of initial ducted fuel injection (DFI) proof-of-concept experiments, showing the potential benefits of the technology for sustaining LLFC at engine loads above ~20%. These initial results show that DFI can be highly effective at preventing soot formation over a range of typical diesel engine conditions and does not require an oxygenated fuel; and (3) showed that the equivalence ratio at the flame lift-off length and the aromatic content of the fuel correlate much more strongly with soot emissions than the liquid phase fuel penetration length. This result supports the idea that the volatility of a new fuel is less important for soot emissions than its ignition quality and aromatic content.

FY 2017 activities: (1) continue to explore DFI to obtain a better understanding of its governing parameters and sensitivities, and to identify the knowledge gaps that should be bridged to enable continued improvement of the technology so that it can be deployed in production engines; (2) conduct a modeling study to determine the likely origin(s) of hydrocarbon emissions from conventional mixing-controlled compression ignition combustion; results will have implications as to whether DFI likely holds promise for lowering hydrocarbon emissions and increasing combustion efficiencies in addition to lowering soot emissions; (3) overcome problems with fuel solidification and conduct optical engine experiments on the certification fuel target fuel and the set of corresponding diesel surrogate fuels described in the FY 2015 report for this project, to determine the level of surrogate fuel compositional accuracy required to adequately match the target fuel combustion performance; and (4) further develop a laser-induced incandescence diagnostic that can provide semi-quantitative, planar images of the in-cylinder soot volume fraction distribution and the total in-cylinder soot mass as functions of crank angle.

- **National Renewable Energy Laboratory** is developing a new experimental method for providing early-stage feedback to biofuel production research and development by identifying promising fuel candidates based on prediction of common autoignition metrics. **(Fioroni, report III.6)**

FY 2016 accomplishments: (1) completed the design and fabrication of an atmospheric pressure small-volume reactor; (2) achieved goal of mapping species profiles across the temperature range (950 K–1,200 K) using 1 mL or less of fuel (typically 0.5 mL or less); (3) determined that the approach using a molecular beam mass spectrometer was not completely adequate to resolve and identify all species and added a gas chromatograph–mass spectrometer to the system for more definitive analysis of reaction products; (4) developed an initial model based on the analysis of primary reference fuel (PRF) and toluene primary reference fuel (TPRF) for the prediction of Research Octane Number and sensitivity (predicted to within 12 to 20 octane number units; and (5) designed a reactor that can operate under elevated pressures up to 10 atm; initial design failed to hold pressure, and a second more robust design was developed

FY 2017 activities: (1) complete an extensive analysis of experimental observables for a larger set of PRF, TPRF, and TPRF–ethanol blends to build an improved Research Octane Number and sensitivity prediction model; (2) develop a simple and rapid approach for measuring residence time distribution in the reactor to assist in modeling of the results; (3) continue development of a reactor that can operate at higher pressures, with an initial target of operation of 10 atm, but with a goal of reaching 30 atm.

- **Argonne National Laboratory** is developing the capability, using a rapid compression machine (RCM)-based device, to experimentally quantify and thereby rank the autoignition properties for a wide range of high and low octane fuels using very small fuel quantities. **(Goldsborough, report III.7)**

FY 2016 accomplishments: (1) a new testing protocol was conceived and validation tests conducted over a range of primary reference fuel (PRF) and toluene reference fuel (TRF) blends at thermodynamic conditions typically experienced in the ASTM octane rating test protocol, as well as beyond; (2) the autoignition measurements of the PRF blends were successfully correlated to trends observed at Research Octane Number (RON) test conditions; and (3) design constraints were established to scale down the RCM geometry in order to reduce the fueling requirements, while at the same time increasing the throughput of the device to achieve the target goals

FY 2017 activities: (1) additional measurements and insight are necessary in order to understand differences between the two different octane rating tests, i.e., RON and Motor Octane Number (MON), and how the autoignition measurements in an RCM-based device can be extended beyond the initial correlation of the PRF blends at the RON conditions; (2) fuels beyond the initial surrogate fuel matrix should be employed in order to quantify the influence of sensitivity (i.e., $S = \text{RON} - \text{MON}$) within the new testing protocol; and (3) the approach to utilize a scaled-down RCM to evaluate potential future fuels has demonstrated good promise with the possibility of extending the measurements to future advanced compression ignition fuel metrics and a prototype should be fabricated and commissioned.

- **Lawrence Livermore National Laboratory** is accelerating the discovery of high performance transportation fuels by developing a measurement process that rapidly screens small sample volumes based on their expected engine performance. **(McNenly, report III.8)**

FY 2016 accomplishments: (1) completed μFIT measurements for three primary reference fuel blends to show that the device has sufficient sensitivity to the fuel composition, and that the ignition and extinction temperatures are correlated to the fuel reactivity (Figure 4); (2) developed a detailed thermal model of μFIT that includes temperature dependent material properties and non-gray body radiation for the quartz tube and thermocouple; and (3) created and tested an improved wall temperature measurement technique that increases the accuracy beyond what is attainable with a thermocouple.

FY 2017 activities: (1) develop a detailed chemical kinetic model of the unsteady flame dynamics in the μFIT system using LLNL's high performance chemistry solver Zero-RK; (2) validate the adiabatic laminar flame speed predictions made using the μFIT measurements combined with unsteady flame simulations; (3) measure small volume fuel samples for the High Performance Fuels Team within the Co-Optimization of Fuels & Engines program; and (4) extension beyond the current scope of the experimental research was selected for contract negotiations for the Co-Optima University Call (DE-FOA-0001461).

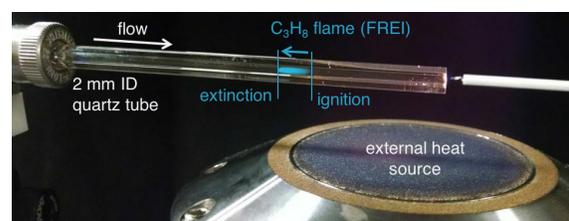


Figure 4. Experimental setup for μFIT operating with a propane and air flame in the unsteady Flames with Repetitive Extinction and Ignition mode. The time needed for the flame to propagate from the ignition point to the extinction point is much less than the exposure time resulting in the appearance of a broad flame. (McNenly, report III.8)

Co-Optimization of Fuels and Engines: Fuel Kinetics and Simulation

This section details the development and application of modeling capabilities to provide crucial insights into the fuel property impacts on engine performance. These physics-based models extend the range, confidence, and applicability of engine experiments.

- **Pacific Northwest National Laboratory** is developing a fuel blending model based upon analytical approaches correlating molecular structure of fuel components to fuel properties and performance, generating a predictive tool for integration into a fuel properties database. **(Bays, report IV.1)**

FY 2016 accomplishments: (1) developed strong chemical structure–property correlations for derived cetane number, T10, T50, and T90 based on one-dimensional nuclear magnetic resonance analyses of 24 gasoline boiling range fuels from bio-derived upgrading processes using regression modeling methods; (2) explored property optimization methods, laying the groundwork for a fuel property blending model; (3) tested diesel fuel surrogates and diesel fuels at pressures up to 380 MPa (~55 ksi) to assess fuel phase behavior at pressures reflecting those found in modern common rail diesel fuel injection systems; and (4) continued collaborative efforts with Coordinating Research Council (CRC) through participation in the Fuels for Advanced Combustion Engines (FACE) Working Group, and contributions to CRC Projects: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling (AVFL-18a), Data Mining of FACE Diesel Fuels (AVFL-23), and Measuring Fuel Heat of Vaporization (AVFL-27).

FY 2017 activities: (1) refine structure–property correlations and develop additional correlations using available and new fuel sets; (2) identify key molecular structures in unconventional fuels, which have the greatest impact on fuel properties and performance; (3) introduce additional fuel sets, including diesel, gasoline, and bio-derived fuels/fuel components, to broaden the applicability of fuel structure–property correlations; (4) continue to examine the high-pressure phase behavior of complex fuels and fuel blends to ascertain the structural origins of high-pressure phase behavior; and (5) continue collaborative work with members of the CRC’s FACE Working Group and the Alternative and Surrogate Fuels projects.

- **Lawrence Livermore National Laboratory** is developing chemical models and associated correlations to predict the blending behavior of bio-derived fuels when mixed with conventional fuels like gasoline and diesel fuels. (**Pitz, report IV.2**)

FY 2016 accomplishments: (1) predicted Research Octane Number for a series of compounds in different chemical classes (e.g., n-alkanes, alkenes, aromatics, cycloalkanes, alcohols) and traced the chemical kinetic origin of octane sensitivity; and (2) demonstrated the ability to compute Research Octane Number for mixtures of ethanol with gasoline surrogates consisting of iso-octane, n-heptane (primary reference fuel); and toluene, iso-octane, and n-heptane (toluene primary reference fuel).

FY 2017 activities: (1) Predict octane blending behavior of two to three classes of advanced performance fuels with two to three core gasoline fuels; and (2) predict blend behavior for candidate advanced performance fuels in core fuels at advanced spark ignition and advanced compression ignition engine conditions.

- **Lawrence Livermore National Laboratory** is developing chemical kinetic models for bio-derived blendstocks and base fuels (e.g., gasoline and diesel) to determine their behavior at advanced spark ignition and advanced compression ignition conditions for Co-Optima. (**Pitz, report IV.3**)

FY 2016 accomplishments: (1) developed chemical kinetic surrogate model for the three Co-Optima core fuels to be used for fuel property hypothesis studies; (2) developed a gasoline surrogate mixture model for E10 RD5-87 gasoline; (3) developed a preliminary chemical kinetic model for anisole (Figure 5); and (4) validated a gasoline surrogate mechanism with ethanol by comparing simulated ignition delay times with measured ignition delay times in the Argonne National Laboratory rapid compression machine for Coordinating Research Council Fuels for Advanced Combustion Engines Gasoline F with varying amount of ethanol.

FY 2017 activities: (1) develop chemical kinetic models for bio-derived blendstocks relevant to advanced compression

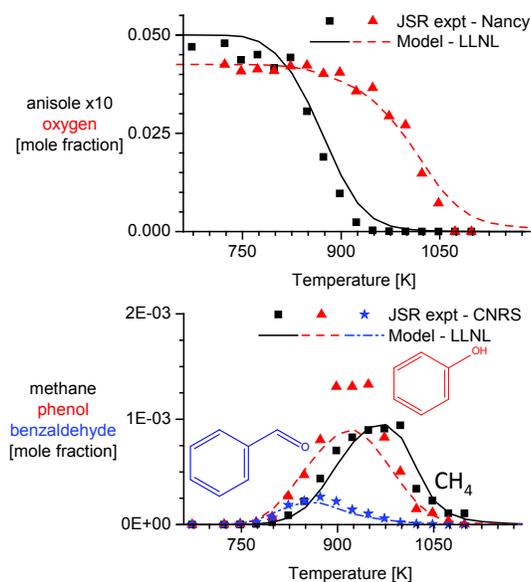


Figure 5. Comparison of simulated and measured species mole fractions in a jet-stirred reactor (JSR) for anisole/O₂/N₂ stoichiometric mixtures at 1 atm. (Pitz, report IV.3)

ignition engine conditions; and (2) predict blending behavior of down-selected bio-blend stocks with Co-Optima core fuels under relevant engine conditions.

- **Argonne National Laboratory** is acquiring autoignition data for a variety of real and surrogate fuels using Argonne's Rapid Compression Machine facilities, at conditions relevant to boosted spark-ignition and advanced compression ignition engines, necessary for the development and validation of detailed and reduced chemical kinetic models. **(Goldsborough, report IV.4)**

FY 2016 accomplishments: (1) acquired new data for primary reference fuel blends and interacted with the Lawrence Livermore National Laboratory (LLNL) fuel properties team members to validate and improve the performance of the LLNL gasoline surrogate model.

FY 2017 activities: (1) measurements will be undertaken with other gasoline surrogate blends, future fuel candidates, and blends of these with surrogate mixtures and full boiling range fuels, so that synergistic and antagonistic behaviors can be quantified and better understood.

- **National Renewable Energy Laboratory** is developing experimental and simulation tools to characterize fuel ignition behavior in support of advanced combustion engine development, both spark ignition and compression ignition. **(Zigler, report IV.5)**

FY 2016 accomplishments: (1) experimentally mapped and simulated parametric ignition delay data for various blends of iso-octane/ethanol, providing critical data to evaluate linking of kinetic mechanisms for blends; (2) demonstrated the non-linear behavior of ethanol blends into iso-octane for low temperature heat release and the negative temperature coefficient region; (3) developed and validated a multizone modeling strategy for Ignition Quality Tester (IQT) simulations to evaluate kinetic mechanisms against experimental data; (4) disseminated research with journal publications in *Fuel* and *Energy & Fuels*; and (5) commissioned and completed initial characterization of a flexible new Advanced Fuel Ignition Delay Analyzer (AFIDA), a National Renewable Energy Laboratory internally funded equipment purchase, to expand beyond IQT-based ignition kinetics studies.

FY 2017 activities: (1) increase small volume ignition delay screening evaluations of candidate compounds under Co-Optima; (2) expand parametric ignition kinetics studies to blends with down-selected candidate compounds under Co-Optima, using the methodology established with ethanol baseline studies, enabling faster kinetic mechanism development and validation; (3) perform modified Livengood–Wu knock integral calculations with IQT and AFIDA data in simulations of engine cycle data at knock limited conditions, establishing links between bench scale ignition delay studies and single-cylinder engine studies; and (4) correlate parametric ignition delay studies with fuel composition for full boiling range gasoline research fuel blends, enabling subsequent correlation providing information beyond Research Octane Number and sensitivity to broader spark ignition boosted engine performance studies.

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. 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.

- **Ford Motor Company** is formulating 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. **(Gangopadhyay, report V.1)**

FY 2016 accomplishments: (1) system level industry standard thermal oxidative stability testing (ASTM D5704) was completed for the most promising oil soluble PAG (OSP) and Generation II PAG formulations and passed; (2) system level industry standard shock load testing (ASTM D7452) was completed for the most promising OSP formulations but failed; (3) Dow Chemical Company and Ford Motor Company (FMC) analyzed the deficiencies of the OSP formulations that failed shock load testing, and optimized the formulations for extreme pressure performance and

antifoam characteristics; (4) Dow and Argonne National Laboratory continued with various laboratory bench screening tests for the OSP formulations; and (5) FMC conducted preliminary efficiency testing on one of the OSP formulations that passed industry standard load carrying capacity testing, that benchmarked PAG performance to 75W-140, confirming efficiency and temperature performance improvements.

FY 2017 activities: (1) complete additional industry standard axle system tests, including load carrying capacity, moisture corrosion, oxidative stability, and shock loading testing with top formulation candidates; (2) complete FMC proprietary axle system (efficiency and gear wear) testing with top formulation candidates; (3) define the best candidate formulation; and (4) complete chassis roll dynamometer tests for fuel economy and emission evaluations.

- **Ford Motor Company** is developing and demonstrating friction reduction technologies for light- and medium-duty vehicles that improve fuel efficiency of future vehicles by at least 4% over currently used technologies based on comparative results from chassis dynamometer testing without adverse impacts on vehicle performance or durability. **(Gangopadhyay, report V.2)**

FY 2016 accomplishments: (1) identified coating deposition parameters that meets targeted plasma transferred wire arc (PTWA) coating porosity levels (6–8%) and established repeatability; (2) identified honing techniques that exceeds targeted porosity levels offering great flexibility; (3) thoroughly characterized coatings for percent porosity, percent oxide content, and hardness; (4) developed manufacturing methodology to deposit coatings on freestanding liners (for laboratory bench tests and characterization), liners (for component level friction tests), and engine blocks (for engine friction tests); (5) initial laboratory bench tests showed up to 50% reduction in friction coefficient in mixed lubrication regime; (6) nano-composite vanadium nitride (VN)–Cu coating deposited on piston rings; laboratory bench friction and wear tests conducted with two different engine oil formulations (Figure 6); and (7) demonstration of friction reduction potential of micro-polished crank journal in-progress with GF-5 oil and polyalkylene glycol engine oils using a motored cranktrain rig.

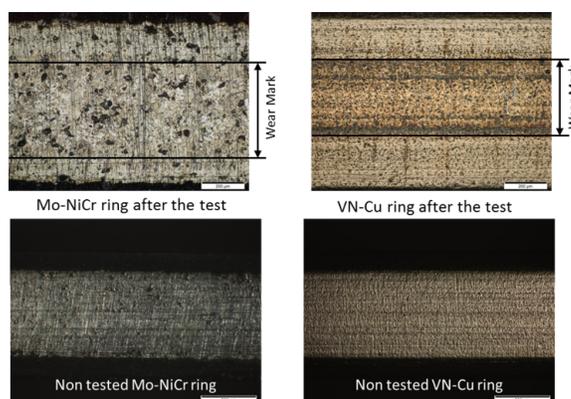


Figure 6. Wear comparison of the rings coated with VN–Cu nano-composite and Mo–NiCr coatings (Gangopadhyay, report V.2)

FY 2017 activities: (1) repeat laboratory friction tests to understand if pore size distribution influences friction reduction; (2) demonstrate if VN–Cu nano-composite coating on rings offer friction reduction in contact with PTWA coated liners; (3) quantify friction reduction with micro-polished crank journals; (4) demonstrate friction reduction in pressurized single-cylinder engine; (5) demonstrate friction reduction in multi-cylinder engine block (cranktrain rig); and (6) initiate wear assessment of PTWA coating in motored engine tests.

- **University of Tennessee** is developing hybrid nanoparticle (NP) lubricant additives for friction and wear reduction to improve engine energy efficiency via synergistic combination of NPs with oil-soluble ionic liquids (ILs), organic ligands, and polymer brushes. **(Zhao, report V.3)**

FY 2016 accomplishments: (1) synthesized oil-soluble IL-functionalized silica NPs (IL-SiO₂NPs) and achieved ~50% friction reduction and ~80% wear reduction at ambient conditions when 1% IL-SiO₂NPs were added into polyalphaolefin (PAO); (2) developed oil-soluble polymer-grafted silica and titania NPs (hairy NPs) that exhibited long-term stability in PAO at –20°C, 22°C, and 100°C (355 d) and demonstrated significant friction reduction (up to ~40%) and wear reduction (up to ~90 %) with the addition of 1% hairy NPs into PAO; (3) synthesized 1–6 nm organic ligand-functionalized silver NPs and achieved up to 35% friction reduction and 80% wear reduction by adding silver NPs (≤0.5%) to PAO; and (4) revealed the dependence of tribological effect of NPs on the ratio of NP size to the initial surface roughness of counter surfaces by computer simulations.

FY 2017 activities: (1) investigate the effect of polymer chemical composition on hairy NPs' tribological performance; (2) develop IL-functionalized NPs and hairy NPs that exhibit improved lubricating properties and long-term stability in PAO; (3) explore different types of core NPs for preparing hybrid NP additives; and (4) elucidate lubrication mechanisms of hybrid NPs by both experimental and modeling studies.

- **George Washington University** is developing GF-6A (backward compatible) 0W-20 fuel efficient lubricant formulation that is at least a 2% fuel economy improvement over a 5W-30 2014 GF-5 commercial oil (baseline) using the GF-6 specification engine sequence test available at the time of milestone due date; this can be used for the legacy fleet vehicles. **(Hsu, report V.4)**

FY 2016 accomplishments: (1) conducted two repeat ASTM Engine Sequence VI-E tests on the 0W-20 formulation that was tested during the fourth quarter of FY 2015 to establish statistical confirmation of the engine test result of 2.39% fuel economy improvement (there was no national test statistics at the time on testing); (2) established cooperative arrangements with several additive companies to provide experimental or new concept friction modifiers and viscosity modifiers under a non-disclosure agreement; (3) developed advanced formulations that show superior performance potentials; and (4) developed surface material technologies and being applied to the engine parts. This includes various surface textures and protective films.

FY 2017 activities: GF-6 prototype oils will be shipped to General Motors as the baseline lubricants to conduct engine durability evaluation on the effect of low viscosity on engines. The tests will be designed and conducted by GM.

- **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 V.5)**

FY 2016 accomplishments: (1) synthesized and characterized three major families of heterocyclic friction modifiers (FMs), whose boundary layer (BL) performances were also optimized greatly; (2) designed and conducted the synthesis of the first generations of copolymers as viscosity modifiers (VMs); (3) functionalized the nanoparticles (NPs), demonstrated their good solubility in base oils and plausible friction reduction together with improvements in wear and scuffing resistances of mating surfaces; (4) investigated entanglement and alignment of FM molecules in their surface adsorption and VMs' shear-thinning transition via molecular dynamics simulations; (5) conducted ultra-thin film measurements and verified the reinforcement of the lubricant film in the BL regime; (6) better understood the origins of the significantly improved BL performances by means of microscale nanoscratch experiments and thermodynamic analyses; and (7) trained postdoctoral researchers, graduate, and undergraduate students; three graduated, one with a Masters of Science and two (partially involved) with doctorates.

FY 2017 activities: (1) further improvements of heterocyclic FMs, copolymer VMs, and functionalized NPs; (2) more laboratory tests considering more comprehensive conditions, oil aeration effects, and oxidation stability; and (3) developments of lubricant formulations and industrial verification tests.

- **Valvoline Inc.** 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 V.6)**

FY 2016 accomplishments: (1) reformulated two engine oil candidates with the latest Proposed Category 11 (FA-4) packages and found better tribological performance in the Mini Traction Machine test while the High Frequency Reciprocating Rig and four-ball test results are mixed; (2) at National Renewable Energy Laboratory, reran ISL 8.9 L engine fuel efficiency (FE) test on both candidates and improvements were observed; (3) Candidate 1 – ISL 8.9 L FE testing results: Federal Test Procedure (FTP) cycle FE 1.6%, Supplementary Emissions Test (SET) cycle FE 1.3%; (4) Candidate 2 – ISL 8.9 L FE testing results: FTP cycle FE 1.8%, SET cycle FE 1.4%; (5) two drums each of Candidate 1 and Candidate 2 and four drums of baseline oil were prepared and shipped out for J1321 test; (6) one drum each of the two axle oil candidates along with two drums of baseline were prepared and shipped out for J1321 test; and (7) two drums of the transmission fluid candidate and four drums of baseline were made and shipped out for J1321 test.

FY 2017 activities: (1) finish the ongoing J1321 test; (2) run SLT B engine evaluation test on both engine oils to appraise their durability performance; and (3) conduct FE retention and durability test on all the three types of oils through field test.

- **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 V.7**)

FY 2016 accomplishments: (1) acquired a variety of rings coated with different coatings for evaluation; (2) developed test methodology to simulate scuffing in the lab, a major failure mechanism of concern to industrial collaborators; (3) developed scuffing test methodology and gained understanding of the factors that affect scuffing by performing experiments using the adjustable-angle reciprocating tribometer; and (4) broadened network of industrial collaborators.

FY 2017 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 test results 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.

- **Argonne National Laboratory** is developing advanced coatings, additives, and basefluids that can reduce parasitic friction losses in engines and drivetrains while maintaining or improving the reliability and durability of components. (**Fenske, report V.8**)

FY 2016 accomplishments: (1) measured the rheological and traction properties for low viscosity polyalphaolefin and two advanced mineral basefluids by kinematic, cold crank viscosity, and high temperature high shear viscosity methods (Figure 7); (2) evaluated several encapsulated colloidal additives candidates that reduced both friction and wear compared to many state-of-the-art advanced lubricants; the impact of the encapsulator requires further studies; and (3) modeled the mechanisms involved in the tribological performance of advanced catalytically active coatings and published the results in the journal *Nature*.

FY 2017 activities: (1) evaluate the impact of additives on the performance of advanced mineral basefluid and polyol ester blends; (2) evaluate the effect of an encapsulator on the tribological performance and behavior of different colloidal additive systems; (3) complete the remaining bench tribological studies and develop friction and wear maps illustrating operational ranges of optimized coatings.

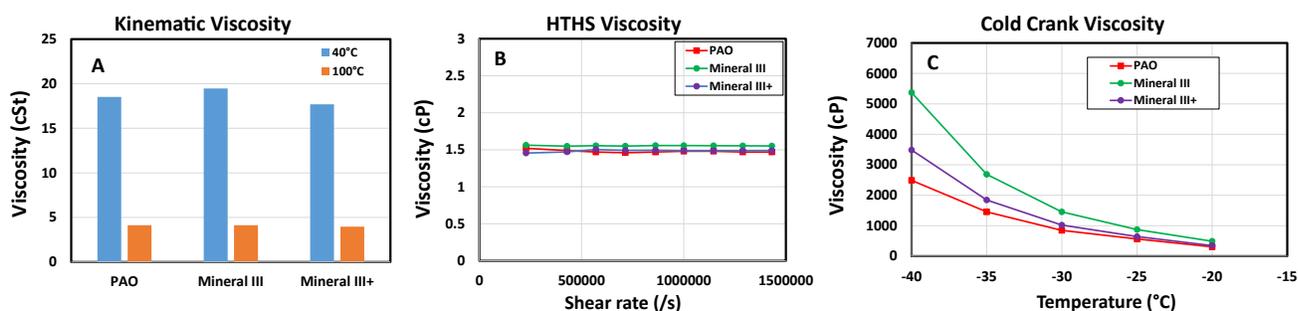


Figure 7. Measurement of basefluids viscosity: kinematic, high temperature high shear (HTHS), and cold crank (Fenske, report V.8)

- **Argonne National Laboratory** is developing a better understanding of the nature (structure), composition, and the mechanisms of formation of tribochemical surface films. (**Ajayi, report V.9**)

FY 2016 accomplishments: (1) observed some deviation in friction for low viscosity fully formulated engine oil; (2) based on optical and scanning electron microscopy, established similarities in scuffing damage from in-use engine components and bench-top test specimen; and (3) in nano-mechanical measurements, determined that tribofilm hardness was 5–7 GPa and varied with thickness; elastic modulus followed a similar trend.

FY 2017 activities: (1) evaluate tribological performance in terms of scuffing and wear under severe contact conditions for additives that produce low friction tribochemical films; (2) continue characterization of the basic mechanisms of scuffing in in-use engine components; (3) in collaboration with academia and industry partners, develop predictive model for wear and scuffing in engine liners; (4) determine and formulate constitutive equations to enable friction prediction and modeling at the lubricated interface; and (5) develop empirical relationship between base fluid viscosity and boundary regime frictional behaviors.

- **Oak Ridge National Laboratory** is improving the understanding of the impact that engine lubricants and fuel properties have on low speed pre-ignition (LSPI) phenomena with a fundamentally focused thermo-chemical parametric fuel and lubricant study. **(Splitter, report V.10)**

FY 2016 accomplishments: (1) demonstrated in-cylinder thermodynamic conditions critical to LSPI event promotion; (2) demonstrated that fuel–wall–lubricant interaction is critical for LSPI cluster event; (3) demonstrated that trapped residual fraction significantly affects LSPI events; (4) disseminated findings to industry and the community through multiple presentations; (5) acquired specific lubricant additives and base stock combinations for LSPI testing; (6) provided all custom lubricants to the National Renewable Energy Laboratory for ignition delay testing; and (7) strengthened strategic partnerships with industry to isolate specific lubricant properties of interest to LSPI; designer lubricants formulated and delivered to Oak Ridge National Laboratory for FY 2017 testing.

FY 2017 activities: (1) evaluate parametric lubricant study of lubricant detergent types on LSPI with and without wall wetting; (2) down-select lubricant properties of interest for further in-depth campaigns; and (3) provide unused and used sump lubricant to the National Renewable Energy Laboratory for ignition delay testing; if successful, couple ignition delay results with statistical LSPI results from engine studies.

- **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 non-ferrous engine bearing alloys, specifically aluminum and bronze alloys that are commonly used in connecting rod end journal bearings and bushings, to gain fundamental understanding to guide future development of engine lubricants. **(Qu, report V.11)**

FY 2016 accomplishments: (1) conducted a series of boundary lubrication tribo-tests on Al–Si and bronze alloys against steel using ZDDP- and ionic-liquid-additized lubricants (Figure 8); (2) friction and wear behavior largely depends on the AW–material combination; Al 380 alloy, ZDDP, phosphate IL, carboxylate IL, and mixture of ZDDP and phosphate or sulfonate IL showed effective wear protection; in contrast, sulfonate IL and mixture of ZDDP and carboxylate IL had significant detrimental impact with the wear rate increased by two orders of magnitude; and (3) performed tribofilm morphology examination and composition analysis to seek fundamental understanding of the lubricant–material compatibility.

FY 2017 activities: (1) continue to explore the effectiveness of AW additives on bronze in boundary lubrication; (2) understand the mechanisms behind the detrimental impact observed on some AW additives when lubricating Al–Si and bronze alloys; and (3) expand the compatibility study to friction modifiers interacting with Al–Si and bronze alloys in mixed and moderate boundary lubrication regimes.

- **Oak Ridge National Laboratory** is ensuring that new fuels and lubricants do not negatively impact emissions and emissions control systems. Specifically, this project investigated: (1) the aging of a three-way catalyst (TWC) with gasoline engine exhaust containing ionic liquid (IL) lubricant additives, and (2) the impacts of start-stop operation

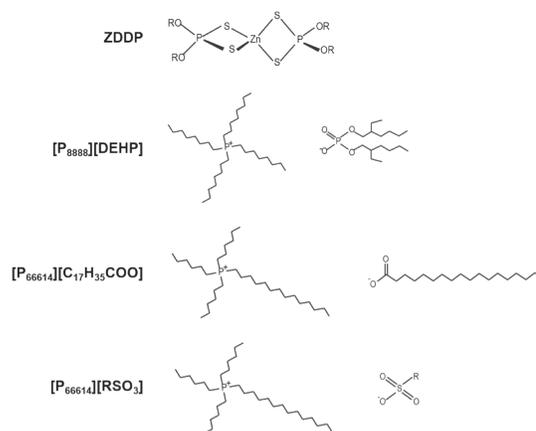


Figure 8. Molecular structures of ZDDP and three ILs used as AW additives in this study (Qu, report V.11)

on particulate matter (PM) emissions from a vehicle equipped with a gasoline direct injection (GDI) engine. (**Storey, report V.12**)

FY 2016 accomplishments: (1) evaluated soot carbon, particle number emissions, and lubricant contributions to PM chemistry from a GDI vehicle operating in start-stop and no start-stop mode over a vehicle drive cycle transient; (2) completed aging experiments of TWC with IL lubricant additives; and (3) finished GDI engine start cart commissioning and started experiments with different viscosity lubricants.

FY 2017 activities: (1) complete data analysis of lubricant viscosity effects on GDI engine PM emissions; and (2) perform additional GDI engine start cart experiments to examine lubricant additive effects on PM emissions.

- **Oak Ridge National Laboratory** is furthering the development of ionic liquid (IL)-additized low-viscosity engine oils meeting the GF-5/6 specifications and possessing superior lubricating characteristics. (**Qu, report V.13**)

FY 2016 accomplishments: (1) submitted two journal papers and gave two invited talks at technical conferences; (2) identified a phosphorus-containing IL to have the best synergistic effects with zinc dialkyldithiophosphate (ZDDP) when used at 1:1 molecular ratio. When combining the IL with a secondary ZDDP, the optimal treat rate was found to have the P content of 400–800 ppm, which well overlaps with the 600–800 ppm regulated by the GF-5/6 specifications; (3) demonstrated more than 50% wear reduction by the IL+ZDDP combination compared with the ZDDP alone when added to a polyalphaolefin 4 cSt base oil at the P level of 800 ppm when tested in boundary lubrication at 150°C; (4) investigated the potential impact of the IL+primary ZDDP combination on three-way catalysts; and (5) designed a rolling-sliding contact fatigue bench test to simulate the lifetime heavy-duty cycles based on contact mechanics and lubrication modeling of the rear axle key contact interface.

FY 2017 activities: (1) formulate a new prototype GF-5/6 SAE 0W-12 engine oil using the top-performing IL+ZDDP combination as the antiwear additive; (2) conduct tribological bench tests and engine dynamometer tests to evaluate the improvement on wear protection and fuel economy; and (3) develop an IL-additized low-viscosity rear axle fluid and demonstrate improved durability and efficiency.

- **Oak Ridge National Laboratory** is designing and developing multi-functional base oils by incorporating chemical and material functionality responsible for one or more of the properties typically provided by lubricant additives, while maintaining or improving lubricant performance. (**Cosimbescu, report V.14**)

FY 2016 accomplishments: (1) completed the study of temperature-induced conformational and size changes using simulations, dynamic light scattering, and small-angle neutron scattering; (2) fundamental study led to the publication of a manuscript that captures all the technical details; (3) achieved the scale-up of three polar base oils and established tribological characterization path with Argonne National Laboratory (ANL) collaborators; (4) demonstrated an increase in shear stability of 50–100% in certain hyperbranched polymers; and (5) demonstrated the value of modeling in predicting viscosity changes with temperature of viscosity modifiers.

FY 2017 activities: (1) finish the synthesis and evaluation of the hyperbranched polymers targeted for shear stability, to enable publishing in a peer reviewed journal; (2) investigate the tribological behavior of Pacific Northwest National Laboratory base oils in collaboration with ANL scientist, to leverage our individual expertise; and (3) publish work generated in collaboration with ANL.

- **Oak Ridge National Laboratory** is developing novel polymers with a branched or hyperbranched architecture as viscosity modifiers. (**Cosimbescu, report V.15**)

FY 2016 accomplishments: (1) generated 11 gal of finished formulated oil; (2) attained the 2013 technical target of a minimum of 2% fuel economy improvement (FEI) in a light-duty vehicle using Pacific Northwest National Laboratory viscosity index improver; (3) demonstrated that the viscosity index improver (VII) can be formulated in a 0W-30 engine oil; (4) conducted blend studies to optimize the concentration of the VII in the finished formulation; (5) worked with collaborators to conduct the Federal Test Procedure which is equivalent to a Sequence VID fuel economy

test; (6) independently, a Sequence VIE fuel economy test was carried out and both tests confirmed a 2% FEI; and (7) published three papers capturing our research.

FY 2017 activities: the project reached an end at the end of FY 2016 and there are no issues remaining. Follow-on work is planned under the lab call funded in FY 2017.

Advanced Fuels and Engines

This section will detail ongoing projects to advance economic and energy security through early-stage research on advanced engines and emerging domestic fuels.

- **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 VI.1)**

FY 2016 accomplishments: (1) completed production of all fuels for the project; (2) commissioned and conducted baseline data collection on a 2.0-L General Motors LTG engine; and (3) conducted vehicle modeling of a mid-size sedan on multiple drive cycles using data from the baseline LTG engine.

FY 2017 activities: identify path forward for calibration of advanced research engine to enable completion of project objectives.

- **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 VI.2)**

FY 2016 accomplishments: (1) applied solid state ¹³C nuclear magnetic resonance to probe shale oil samples, fresh and spent, examining the organic material that was turned into fuel components, as well as the residual organic material remaining in the shale; and (2) continued collaboration with CanmetENERGY and further refined structure–property relationships for diesel fuel lubricity using nuclear magnetic resonance and gas chromatography–field ionization mass spectrometry data.

FY 2017 activities: (1) this project will be closed out and the results for fuels derived from shale oil reported in a publication. Structure–property relationships explored under this project will be continued under Co-Optima.

- **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 VI.3)**

FY 2016 accomplishments: (1) demonstrated 50% petroleum reduction over Ramped Modal Cycle Supplemental Emissions Test cycle (Figure 9); (2) demonstrated 50% petroleum reduction over hot Federal Test Procedure cycle; and (3) built a heavy-duty Class 8 dual-fuel vehicle.

FY 2017 activities: (1) demonstrate petroleum reduction with final emissions capable calibration; and (2) perform vehicle demonstration of the Class 8 dual-fuel vehicle.

- **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 VI.4)**

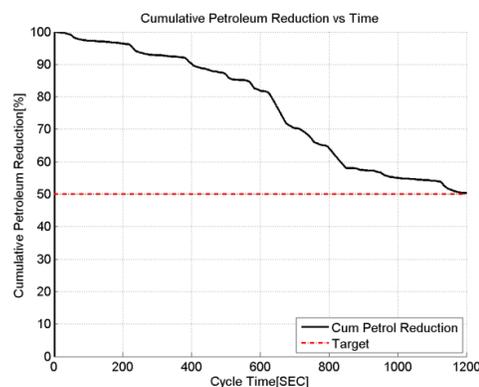


Figure 9. Cumulative petroleum reduction over hot Federal Test Procedure cycle (Kocher, report VI.3)

FY 2016 accomplishments: (1) a GT-POWER model of fuel evaporation was developed with good agreement with experiment data; (2) a detailed kinetic fuel model was used to characterize knock limited load data from the literature; (3) major improvement in the range of maximum brake torque operation of the production single-cylinder engine was demonstrated by blending gasoline with ethanol, with a maximum gross indicate thermal efficiency of 38.4%; (4) a state-of-the-art, production, multi-cylinder gasoline turbocharged direct injection (DI) engine was installed and instrumented for fuel effects studies and a design of experiments was developed and applied to fuel injection and fuel blend studies; (5) approximately four percentage point increase in brake thermal efficiency was achieved with E85 (85% ethanol, 15% gasoline blend) compared with gasoline using the multi-cylinder engine facility; (6) E85 yielded significantly lower exhaust temperatures for the same load conditions compared with gasoline which reduced the losses due to fuel enrichment for component protection; (6) a port fuel injection (PFI) cylinder head was modified for combined DI+PFI operation on a single-cylinder Hydra engine; and (7) a study of the effects of syngas (simulated fuel reformat) addition to gasoline for knock suppression was completed using the Hydra test engine.

FY 2017 activities: (1) complete DI fuel injection controls development and perform combined DI+PFI stratified and multiple-injection DI stratified fueling studies to assess impacts of fueling strategy on knock suppression in the Hydra; (2) assess tradeoffs between particulate mass/particulate number emissions and knock suppression for fueling strategies in the Hydra and the multi-cylinder test engines; (3) evaluation of the in-cylinder soot formation in the multi-cylinder engine using in-cylinder imaging to identify the sources of soot and the effects of alcohols in soot suppression; (4) future engine and fuel modeling work will focus on integrating the models developed so far, calibrating with recent data and projecting possible engine benefits to vehicle fuel economy improvements.

- **Stony Brook University** is reforming gasoline, diesel, and natural gas to varying levels and characterize the constituent species of the reformat mixtures as well as the autoignition tendency of the reformat mixture in the form of an effective Primary Reference Fuel (PRF) number. (**Lawler, report VI.5**)

FY 2016 accomplishments: (1) the test facility was constructed to vaporize and reform gasoline, diesel, and natural gas to varying levels; (2) the modifications to the existing Cooperative Fuel Research engine were made and the PRF mapping was created by igniting blends of n-heptane and isooctane over a wide range of intake temperatures and compression ratios; and (3) gasoline, diesel, and natural gas were reformed to various levels and the constituent species of the reformat mixture were characterized using gas chromatography.

FY 2017 activities: (1) in the following years, an effective PRF number of the reformat mixtures will be determined by autoigniting the reformat mixtures in homogeneous charge compression ignition combustion and comparing their results to the PRF mapping; (2) computational fluid dynamics and GT-SUITE models will be created to evaluate the potential efficiency, emissions, operating range, and burn characteristics of the proposed concept using computational fluid dynamics simulations with detailed chemical kinetics as well as GT-SUITE models; and (3) each parent fuel–reformat combination will then be experimentally tested in reactivity controlled compression ignition (RCCI) and comparisons between reformat RCCI and published RCCI data in the literature will be made.

- **Southwest Research Institute**[®] is quantifying the impact of fuel chemistry and formulation on Dedicated Exhaust Gas Recirculation (D-EGR[®]) hydrogen production. (**Briggs, report VI.6**)

FY 2016 accomplishments: (1) completed modifications to the research engine; and (2) demonstrated hydrogen production of 7% (vs. 3% reported in previous work).

FY 2017 activities: (1) evaluate the impact of petroleum fuel chemistry on hydrogen production; (2) evaluate the impact of biofuel chemistry on hydrogen production; and (3) demonstrate an engine that will achieve a 25% petroleum use reduction relative to a baseline passenger car engine.

- **Argonne National Laboratory** is utilizing 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. (**Goldsborough, report VI.7**)

FY 2016 accomplishments: (1) blended a full boiling-range gasoline with 10 different single component, gasoline-representative molecules at 10% v/v levels, and characterized properties of the blended fuels using Chevron's facilities; (2) acquired autoignition delay and heat release measurements for the 10% v/v gasoline blends in Argonne's twin-piston RCM; (3) acquired performance and emissions data for the 10% v/v gasoline blends using Argonne's prototype gasoline compression ignition (GCI) engine; and (4) further developed correlations for the fundamental RCM measurements which will indicate operational performance within the GCI engine.

FY 2017 activities: (1) blend and characterize the properties of additional fuels at 20% v/v levels using single- and two-component surrogates using Chevron's facilities; (2) acquire autoignition delay and heat release measurements for the 20% v/v 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) based on experimental observations, formulate a measurement protocol which is capable of quantifying fuel sensitivities important for GCI (and other LTC modes) including temperature, pressure, equivalence ratio, and dilution, i.e., exhaust gas recirculation.

- **Argonne National Laboratory** is optimizing combustion concept with targeted in-cylinder natural gas (NG)/gasoline blending to achieve 10% efficiency improvement over gasoline baseline. **(Wallner, report VI.8)**

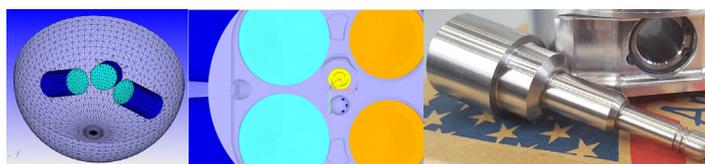


Figure 10. Meshing details and installation study of nozzle tip variant, with machined hardware (Wallner, report VI.8)

FY 2016 accomplishments: (1) successfully designed and implemented increased compression ratio engine options and injector nozzle design based on three-dimensional computational fluid dynamics modeling results (Figure 10) (2) demonstrated 40.9% indicated efficiency with NG direct injection at 12.5:1 compression ratio, exceeding the efficiency in gasoline port fuel injection operation by 11.9%, a ~41% relative improvement; and (3) validated blending concept potential to improve power density achieving an increase in indicated mean effective pressure from 5.8 bar with E10 (10% ethanol, 90% gasoline blend) to 10.2 bar with NG, a relative improvement of more than 75% taking advantage of the high knock resistance of NG at an increased compression ratio of 12.5:1.

FY 2017 activities: (1) implement efficiency and performance characteristics from optimized hardware configurations in the vehicle level analysis; (2) develop a vehicle level strategy with the goal to maximize the global benefits of the in-cylinder blending strategy; and (3) perform vehicle level simulations and a cost analysis evaluating progress towards the 50% petroleum reduction and 36-month payback period goals.

- **Robert Bosch LLC** is developing and demonstrating a High-Efficiency Cost-Optimized Spark-Ignited Natural Gas (HECO-SING) heavy-duty engine capable of approaching current near-diesel efficiency while achieving current Environmental Protection Agency emission regulations. **(White, report VI.9)**

FY 2016 accomplishments: (1) Performed baseline testing on as-received lean burn non-exhaust gas recirculation (EGR) configured engine; (2) initial studies on level of ammonia generation in varied rate EGR and non-EGR configurations, critical to assess feasibility of passive selective catalytic reduction (SCR) concept, performed; (3) project baseline testing performed on engine converted to stoichiometric EGR configuration (representing current state-of-the-industry); (4) detected issues with the original turbocharger sizing and EGR system implementation, and revised design to operate successfully; (5) ignition systems literature review study performed, completed, and presented to DOE representatives; (6) selection of advanced ignition systems to study on the engine accomplished (conventional higher energy ignition, constant energy ignition, corona discharge, and turbulent jet ignition); (7) combustion optical instrumentation designed fabricated; (8) combustion optical and spectroscopic in-cylinder measurement system device and accessories specified and procured; (9) bench top rig created to assess optical measurement capabilities and pre-preparation for engine testing, to quantify ignition systems combustion impacts; (10) began aftertreatment model development; (11) identified and included capturing of engine hydrogen output levels

over the range of operation for input into the aftertreatment model, which was not originally identified in the project submission; (12) catalyst literature review study performed and completed; (13) initial conventional ignition systems combustion limit study performed; and (14) initial assessment of passive SCR (manual mode) engine efficiency performed.

FY 2017 activities: (1) evaluation of the selected advanced ignition systems, assess their impact on combustion through performance and optical measurements, and assess their improvement on engine efficiency; (2) present catalyst literature review study to DOE representatives at Pacific Northwest National Laboratory site visit; (3) site visit to Bosch to witness combustion measurements on engine; (4) analyze effectiveness of aftertreatment model via testing on synthetic gas bench; (5) develop software controls to allow for optimized switching between lean, rich, and stoichiometric operation for passive SCR function; (6) and verification of aftertreatment modeling, engine controls to achieve optimized efficiency and emissions operation, and ignition and fuel systems to achieve those improvements will be performed in the final budget year period.

I.3 Honors and Special Recognitions/Patents

Honors and Special Recognitions

1. 2015 U.S. DRIVE Highlight: “Mechanism for Stabilizing Fuel-Efficient, Stratified SI Operation Identified.” (Sjoberg, report II.4)
2. Selected as one of the Co-Optimization of Fuels & Engines End of Year highlights for FY 2016. (Kolodziej, report II.5)
3. USCAR Recognition Award for contributions to the U.S. DRIVE Advanced Combustion and Emissions Control Fuels Roadmap Sub-Team. (Szybist, report II.6)
4. SAE Forest R. McFarland Award for outstanding contributions in planning, development, and dissemination of technical information. (Szybist, report II.6)
5. Efforts were part of a team recognized as the 2015 Biodiesel Researchers of the Year in November of 2015. Other members: Bob McCormick (National Renewable Energy Laboratory), Richard Ancimer (Cummins), Michael Lance and Todd Toops (Oak Ridge National Laboratory) for collaborative effort investigating the Impact of Metal Impurities on Catalyst Durability. (Toops, report II.9)
6. DOE EERE Special Recognition Award – For research on diesel engine and HCCI-like combustion. Presented by DOE at the Annual Merit Review, June 2016. (Dec, report III.2)
7. USCAR Team Award for work on the U.S. DRIVE ACEC Fuels Roadmap Sub-Team. (Dec, report III.2)
8. Green Car Congress review of gasoline compression ignition review article, <http://www.greencarcongress.com/2016/01/20160118-ornl.html> (Curran, report III.3)
9. C.J. Mueller received a USCAR Team Award for contributions to the U.S. DRIVE Advanced Combustion and Emissions Control Fuels Roadmap Sub-Team (May 26, 2016). (Mueller, report III.5)
10. C.J. Mueller served as co-chair and local host of the 2nd Coordinating Research Council Advanced Fuels and Engine Efficiency Workshop, Livermore, CA (November 1–3, 2016). (Mueller, report III.5)
11. Hongyu Gao – University of California, Merced Spring 2016 Graduate Dean’s Dissertation Fellowship. (Zhao, report V.3)
12. Blake Johnson, Michael Desanker, Jie Lu, and David Pickens, First Place Winners, BASF Science Competition, 2016. (Wang, report V.5)
13. Wang, Q., International Award, STLE, 2015. (Wang, report V.5)
14. Marks, T.J., Luigi Sacconi Medal, Italian Chemical Society, 2015. (Wang, report V.5)
15. Marks, T.J., Derek Birchall Award, Royal Society of Chemistry, 2015. (Wang, report V.5)
16. As a result of this project, the viscosity index improver technology was selected for the Lab Corps Program (Lab Cohort 4). (Cosimbescu, report V.15).

Invention and Patent Disclosures

1. U.S. Patent Application Filed, No. 14/855,809: Dec, J.E, and Renzi, R., September 2015. (Dec, report III.2)
2. U.S. Patent Application #14,789,782: “Ducted Fuel Injection.” Filed/pending July 1, 2015. (Mueller, report III.5)
3. U.S. Patent Application # 15,363,966: “Ducted Fuel Injection.” Filed/pending November 29, 2016. (Mueller, report III.5)
4. U.S. Patent Application # 15,364,002: “Ducted Fuel Injection with Ignition Assist.” Filed/pending November 29, 2016. (Mueller, report III.5)
5. “Low cost thermal spray coating for improved engine performance,” submitted patent application, March 18, 2016. (Gangopadhyay, report V.2)

6. 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 V.5)
7. 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 V.9)

II. Co-Optimization of Fuels and Engines: Light-Duty

The trend toward turbocharging and downsizing/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. Research in this area is working to establish a comprehensive understanding of how fuel properties impact efficiency in boosted, gasoline direct injection engines.

II.1 Alternative Fuels DISI Engine Research – Autoignition Metrics

Overall Objectives

Sandia National Laboratories will provide the science-base needed by industry stakeholders to understand how engine design and operation can be co-optimized with future fuels for highest overall system efficiency.

Fiscal Year (FY) 2016 Objectives

- Use partial fuel stratification to study fuel effects on ultra-lean mixed-mode spark ignition (SI) combustion (with transition from deflagration to autoignition)
- Develop hardware and engine operating strategies that enable optical diagnostics of the transition from deflagration to end-gas autoignition
- Provide experimental data in support of collaborative efforts on detailed chemical kinetics modeling of new fuels and fuel components
- Assess the efficacy of commonly used fuel properties to rank fuels of dissimilar composition in terms of their knock limits for stoichiometric SI engine operation
- Identify and explain fuel-related factors contributing to knock resistance in SI engines

FY 2016 Accomplishments

- Finished a study on the use of partial fuel stratification to stabilize ultra-lean mixed-mode SI combustion for gasoline and E85 (85% ethanol, 15% gasoline blend by volume) fuels over wide load ranges
- Finished a study on the combined effects of intake flow and spark plug location on flame development, combustion stability and end-gas autoignition for lean SI engine operation using E30 (30% ethanol, 70% gasoline blend by volume) fuel; demonstrated the feasibility to apply optical diagnostics of the transition from deflagration to autoignition
- Developed modeling methodology and provided validation data for an extensive chemical kinetics modeling study with Westbrook et al. [1] on the fuel-based origin of octane sensitivity
- Determined steady-state knock-limited combustion phasing (KL-CA50) over ranges of intake pressure and temperature for stoichiometric operation with a compression ratio of 12 using three Co-Optima Core

Magnus Sjöberg (Primary Contact), David Vuilleumier

Sandia National Laboratories
MS9053, PO Box 969

Livermore, CA 94551-0969

Phone: (925) 294-3635

Email: mgsjobe@sandia.gov

DOE Technology Development Manager:
Kevin Stork

Fuels with Research Octane Number (RON) = 98 and dissimilar composition

- Addressed one of the barriers identified by DOE Vehicle Technologies Office: inadequate data for fuel property effects on combustion and engine efficiency optimization

Future Directions

- Expand stoichiometric knock study to higher intake pressures by reducing compression ratio to 10
- Incorporate transient knock testing to increase real-world relevance of results
- Incorporate new fuel components and blends in coordination with other Co-Optima teams
- Measure turbulent deflagration rates optically for key fuel blends and compare results with existing database for laminar flame speed
- Continue examination of well-mixed lean or dilute SI operation while quantifying the relevance of RON and Motor Octane Number (MON) for fuel reactivity under ultra-lean conditions ■

Introduction

The quest for improved engine efficiency is forced by ever stricter fuel economy legislation. At the same time, there is interest to develop alternative fuels that are based on non-petroleum sources. This creates an opportunity to develop a new gasoline-type fuel that enables both higher engine and system efficiencies. This project contributes to the science-base needed by industry stakeholders to assess

the merit of alternative fuel formulations. Specific interest is paid to the effects of fuel properties and formulation on engine combustion and efficiency, and in particular to knock-limited SI combustion. When specifying new fuels standards, it is crucial to understand whether fuel properties and specifications are sufficient to describe their behavior, or whether their molecular composition must be considered as well. This research contributes to the knowledge base needed to make decisions about future fuel formulations.

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 wide ranges of operating conditions and alternative fuel blends. Second, in-cylinder processes are examined with high-speed optical diagnostics, including advanced laser-based techniques. Computer modeling also provides insight into the governing combustion fundamentals. The combination of performance testing, exhaust emissions measurements, optical diagnostics, and modeling supports building a comprehensive science-base.

Results

In the following, examples of accomplishments during FY 2016 are presented.

Lean Mixed-Mode SI Operation

Lean or exhaust gas recirculation diluted operation can improve the thermal efficiency relative to throttled stoichiometric operation, but the fuel economy gains depend on several factors. These include fuel type, dilution type, and intake temperature, as documented in a recent study [2]. Maintaining the 10–90% burn duration below 30° crank angle is a requirement if fuel economy gains are to be realized, and this is one of several challenge associated with lean operation [3]. Mixed-mode combustion can ensure a short burn duration by utilizing autoignition of the end-gas located ahead of the turbulent flame [2]. Increased combustion noise is a concern, but local heat release rates of the autoigniting end-gas can be maintained acceptably low by utilizing high dilution rates and stable deflagration. Even so, the transition from deflagration to autoignition is not well understood, prompting optical engine studies. However, with a conventionally located spark plug near the center of the combustion chamber, the transition from deflagration to autoignition occurs at the periphery of the combustion chamber, which makes it challenging to achieve

meaningful optical diagnostics. To overcome this, two additional spark plugs were installed in the current direct injection spark ignition (DISI) engine. With one spark plug in each pent-roof gable, the ensuing two turbulent flame fronts compress a centrally located end-gas volume. This makes it possible for the transition from deflagration to autoignition to occur in a central region of the combustion chamber, as depicted in Figure 1. The high-speed imaging presented in this figure uses an E30 blend with a high RON of 105. It can be observed that the second apparent heat release rate (AHRR) peak corresponds well to a brief period of increased chemiluminescence in the nine o'clock direction. Once the autoignition-based combustion has finished, the AHRR trace falls rapidly towards zero, indicating that essentially all remaining fuel was consumed rapidly despite the low ϕ of 0.55.

Using a well-mixed charge, it can be difficult to realize stable combustion for ultra-lean operation. By injecting a small amount of fuel near the spark plug at the time of ignition, partial fuel stratification is realized. This stratification can ensure stable deflagration even for $\phi < 0.55$. Engine testing with a high-octane certification gasoline and E85 shows that very stable mixed-mode combustion can be achieved for operation with a low global ϕ of 0.38. These results indicate that a combination of well-mixed and partially stratified operation can be used to cover wide load ranges with efficient unthrottled lean SI engine operation, even for high-RON fuels.

RON- and MON-Like Operation

As discussed previously, lean operation can benefit from end-gas autoignition. Conversely, for stoichiometric SI operation (discussed more in the next section) end-gas autoignition should be avoided since it causes engine knock. To support the effective development of both lean-burn and stoichiometric engine combustion systems, computer models which accurately predict the effect of fuel composition are required. In support of a collaborative chemical kinetics modeling study aimed at explaining the fundamental origin of fuels' RON-MON octane sensitivity, the DISI engine was operated in two different ways to resemble the RON and MON tests used to rank the anti-knock quality of fuels. Specifically, for the RON-like condition, the engine speed was set to 600 rpm and no intake heat was used. For the MON-like condition, the engine speed was 900 rpm, and strong intake air heating was applied. The well-characterized engine operation allows the in-cylinder temperature to be computed fairly accurately. Figure 2 shows the different temperature–pressure (T-P) trajectories of the RON- and MON-like operation. For the RON-like operation, the pressure is much higher at a given temperature of the end-gas reactants. In addition, the traverse in T-P space

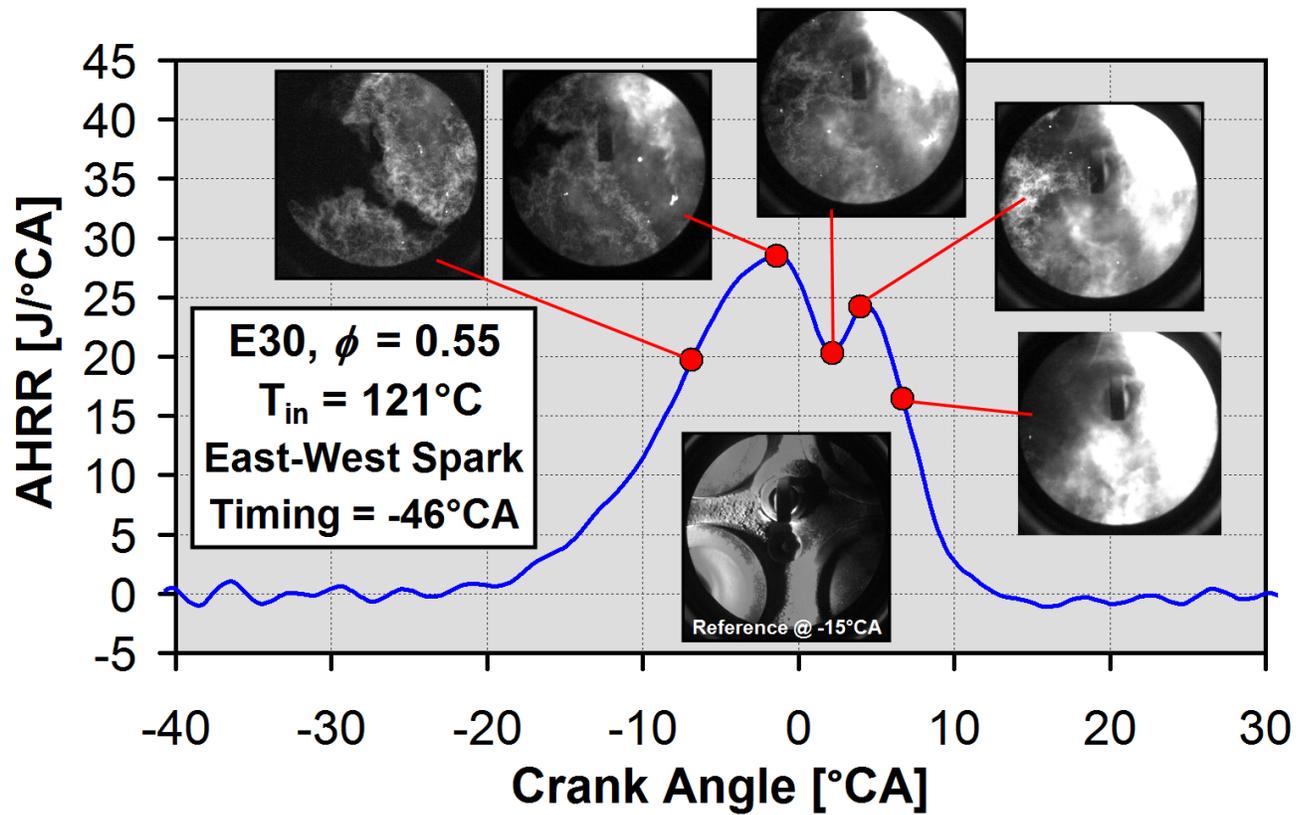


Figure 1. AHRR and flame imaging of transition between turbulent deflagration and end-gas autoignition for lean E30 operation with two gable-mounted spark plugs

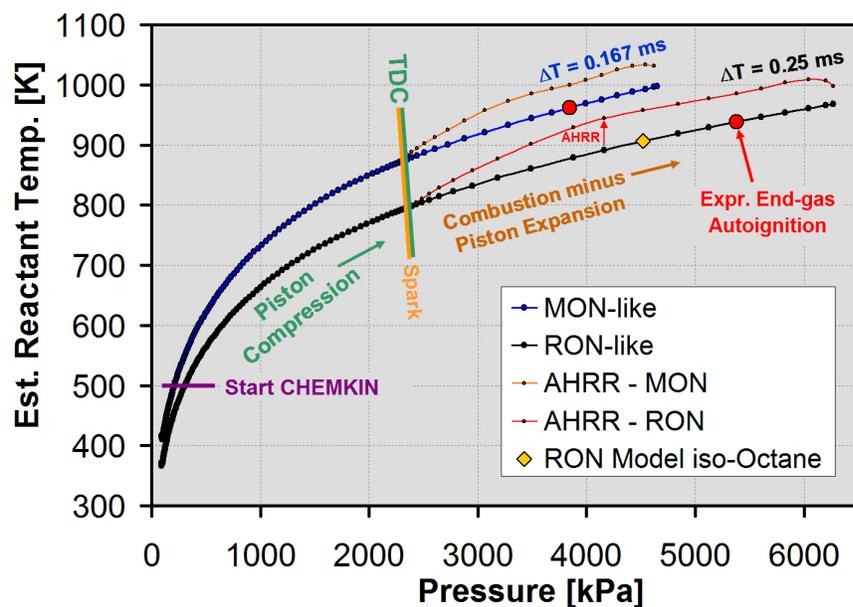
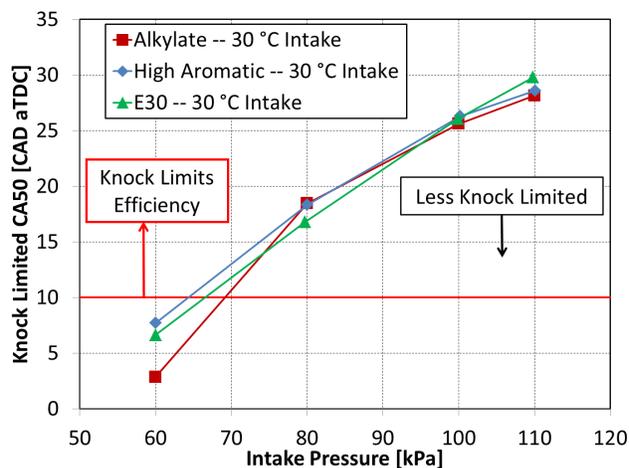


Figure 2. Experimentally derived temperature–pressure histories for RON- and MON-like engine operation used as input to Chemkin-Pro modeling. Red circles indicate experimentally determined autoignition timing. Yellow diamond indicates an example result from Chemkin-Pro modeling, here for iso-octane with RON = 100 < 105 of E30 used experimentally.

is slower, as indicated by the longer ΔT between data points. Both of these factors contribute to an increased importance of low-temperature heat release (LTHR) for the RON condition. For Chemkin-Pro modeling of end-gas autoignition, the model was initiated as a homogeneous reactor with a pressure corresponding to the T-P trajectory at 500 K. From this point in time, the model was fed the experimentally measured pressure as a function of time. The fuel used for the experiment was E30 with a RON of 105. Consistent with this, the model prediction for iso-octane (RON = MON = 100) shows an autoignition event (yellow diamond) that occurs ahead of the experimentally observed end-gas autoignition (red circle). These T-P trajectories were used to support an extensive modeling study on the origin of RON-MON sensitivity as discussed elsewhere in report IV.2, “Fuel Property Blending Model,” by William J. Pitz, and in Westbrook et al. [1].

Stoichiometric Knock Limits with Co-Optima Core Fuels

The efficiency of stoichiometric SI operation is often limited by the unwanted autoignition of the end-gas reactants. The resistance of a fuel to autoignition is often described by its RON or MON. A central hypothesis of the Co-Optima effort is that engine performance can be adequately described by common fuel property metrics. In terms of knock-limited SI engine performance, those metrics are primarily RON, MON, and heat of vaporization, without regards to fuel composition. In order to assess one aspect of this central fuels hypothesis, three RON = 98 fuels were tested for their autoignition resistance via KL-CA50 sweeps. These three fuels have been dubbed the Co-Optima Core Fuels, and differ by composition and MON numbers. (See Table 1 in report II.4, “Alternative Fuels DISI Engine Research – Stratified Lean and Homogeneous Lean,” by Magnus Sjöberg.) The alkylate fuel has a MON of 97 and consists of paraffins. The high-aromatic gasoline and E30 fuels both have MON \approx 87, and contain \approx 30% aromatics or ethanol, respectively. Figure 3 presents results from an intake pressure sweep of the three fuels at a constant intake temperature. This figure shows that the fuels generally exhibit similar knock resistance to one another, except at low intake pressure where the high MON of the alkylate provides a benefit. This behavior fits well with the fuels’ identical RON ratings and previous work relating RON and MON ratings to knock resistance in SI engines, especially the use of the Octane Index to describe the observed knock resistance [4]. Although the fuels exhibit similar KL-CA50 behavior near naturally aspirated conditions ($P_{in} \approx 100$ kPa), the mechanisms of knock resistance for the three fuels vary. One indication of this

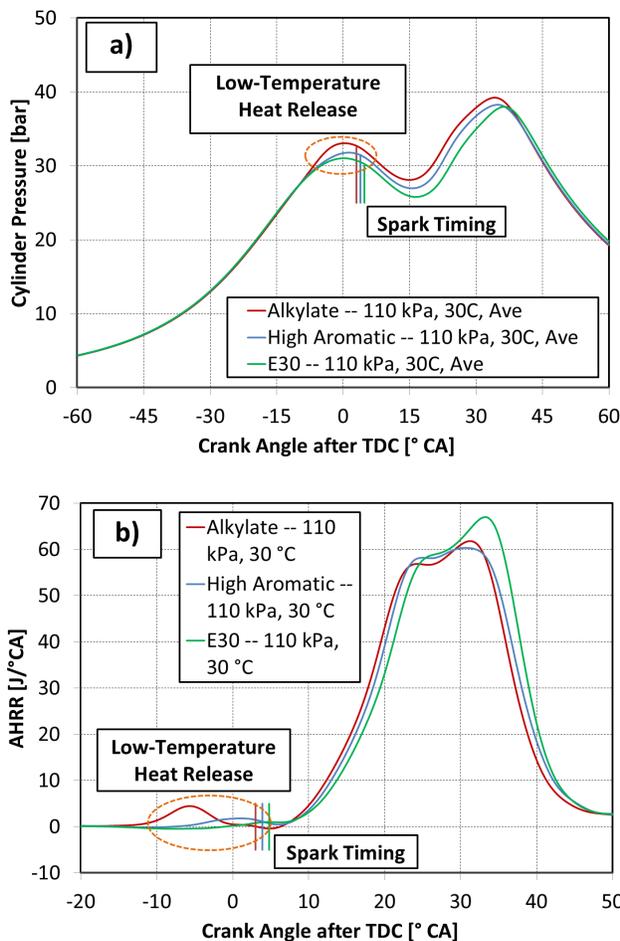


CAD – crank angle degrees; aTDC – after top dead center

Figure 3. KL-CA50 behavior of the three tested fuels for stoichiometric operation at 1,400 rpm with an intake temperature of 30°C

is the difference in the amount of LTHR, as shown in Figure 4b. The alkylate fuel has a distinguished LTHR bump prior to the spark timing, and the high-aromatics fuel has some LTHR. In contrast, the E30 fuel shows minimal levels of LTHR.

Figure 5 plots the T-P trajectories of the end-gas leading up to the point of autoignition for two intake pressure conditions per fuel. The differences in trajectories at a fixed intake pressure yield indications as to the mechanisms underlying autoignition resistance for each fuel. Further, the differences between the 60 kPa and 110 kPa intake pressure conditions indicate the effects of intake pressure on each fuel. The autoignition resistance of each fuel was found to depend primarily on three factors: the ultimate thermal autoignition resistance of the fuel, the amount of charge heating caused by the fuel’s LTHR, and the degree of charge cooling caused by the evaporation of a stoichiometric mass of fuel into air. The E30 fuel’s autoignition resistance is derived from the lack of LTHR and greater evaporative charge cooling than the other two fuels; however, the E30 fuel autoignites at the lowest temperatures of the three fuels. Conversely, the alkylate fuel exhibits the greatest amount of LTHR, but also exhibits the greatest thermal resistance. These two factors balance at the 100 kPa intake pressure condition to provide the same performance as the other two fuels, see Figure 3. Meanwhile, at the 60 kPa intake pressure condition the fuels do not exhibit LTHR. Consequently the alkylate fuel’s greater thermal resistance yields the best performance at low intake pressures.



TDC – top dead center

Figure 4. Ensemble-average (a) pressure traces and (b) calculated AHRR traces of the three tested fuels at KL-CA50 conditions with 110 kPa intake pressure and 30°C intake temperature

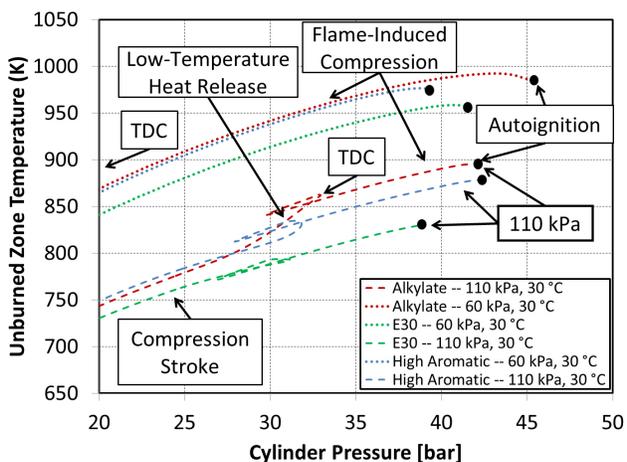


Figure 5. Temperature and pressure histories of the end-gas of the reacting charge leading up to the point of autoignition for the three tested fuels at 60 kPa and 110 kPa intake pressures

Conclusions

- Use of partial-fuel stratification allows stable mixed-mode SI operation over wide load ranges, enabling studies of end-gas autoignition even for ultra-lean conditions.
- Engine operation with one spark plug in each pent-roof gable enables optical diagnostics of the transition from deflagration to autoignition, providing opportunities for future research.
- Experimental data generated by RON- and MON-like engine operation support detailed chemical kinetics modeling to determine the fundamental origin of RON-MON sensitivity.
- For stoichiometric SI operation at naturally aspirated and throttled conditions, knock resistance of three Co-Optima Core Fuels is well described by their RON and MON ratings.
- Despite identical RON, the three compositionally dissimilar Co-Optima Core Fuels exhibit key differences in terms of evaporative cooling, LTHR, and ultimate thermal resistance.

References

1. C.K. Westbrook, M. Mehl, W.J. Pitz, and M. Sjöberg, "Chemical kinetics of octane sensitivity in a spark-ignition engine", *Combustion and Flame*, Volume 175, January 2017, Pages 2-15, doi:10.1016/j.combustflame.2016.05.022.
2. Sjöberg, M. and Zeng, W., "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," *SAE Int. J. Engines* 9(2):750–767, 2016, doi:10.4271/2016-01-0689
3. Ayala, F., Gerty, M., and Heywood, J., "Effects of Combustion Phasing, Relative Air-fuel Ratio, Compression Ratio, and Load on SI Engine Efficiency," *SAE Technical Paper* 2006-01-0229, 2006, doi:10.4271/2006-01-0229.
4. G. Kalghatgi, "Fuel Anti-Knock Quality - Part I. Engine Studies," *SAE Technical Paper* 2001-01-3584, 2001.

FY 2016 Publications/Presentations

1. M. Sjöberg, W. Zeng and Z. Hu, "Combined Effects of Fuel Type, Load Level and Intake Temperature on the Use of Controlled End-gas Autoignition to Enable Ultra-lean SI Engine Operation," presented at AEC Program Review Meeting at Sandia, February 2016.

2. 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,” presented at SAE Congress and published in SAE International Journal of Engines, 2016.
3. C.K. Westbrook, M. Mehl, W.J. Pitz, and M. Sjöberg, “Chemical Kinetics of Octane Sensitivity in a Spark-Ignition Engine,” Combustion and Flame, 2017.
4. M. Sjöberg and X. He, “Combined Effect of Intake Flow and Spark-Plug Location on Flame Development, Combustion Stability and End-gas Autoignition for Lean SI Engine Operation using E30 Fuel,” presented at AEC Program Review Meeting at USCAR, August 2016.
5. D. Vuilleumier and M. Sjöberg, “Co-Optima Core Fuels: Initial Investigations of Knocking Behavior in a DISI Engine,” presented at AEC Program Review Meeting at USCAR, August 2016.

Acknowledgements

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

II.2 Studies of Research Octane Number (RON) and Heat of Vaporization (HoV)

Overall Objectives

- Investigate the effects of fuel properties on the characteristics of mixture auto-ignition using a well-instrumented CFR F1/F2 fuel octane rating single-cylinder research engine
- Quantify the impact of fuel HoV on measured RON
- Develop a strategy to decouple HoV from measured RON

Fiscal Year (FY) 2016 Objectives

- Instrument and commission a CFR F1/F2 fuel octane rating engine to make modern engine combustion research measurements
- Characterize the effect of standard primary reference fuel (PRF) octane number on RON testing engine operating conditions
- Compare the effect of increased HoV of ethanol-PRF blends to standard PRF fuels on RON rating

FY 2016 Accomplishments

- Installed, instrumented, and commissioned a CFR F1/F2 fuel octane research engine
- Created one-dimensional (1D) GT-POWER model of CFR F1/F2 engine to calculate cylinder pressure and temperature conditions
- Developed a matrix of PRF-ethanol fuels to yield matched RON 98 for ethanol blends up to 50%
- Characterized differences in lambda at peak knocking condition between standard PRF fuels and PRF-ethanol blends, with peak knocking occurring at 0.9 lambda for PRF fuels and 0.95 lambda for PRF-ethanol blends
- Established that the HoV effect of 50% ethanol exceeds 1 RON unit

Future Directions

- Validate 1D GT-POWER engine model to determine how fuel HoV affects cylinder pressure and temperature during RON measurement
- Quantify the effect of ethanol HoV in full boiling range gasolines and expand on PRF-ethanol results

Christopher P. Kolodziej (Primary Contact), Thomas Wallner, Andrew Ickes, Seungmok Choi

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
Phone: (630) 252-1599
Email: ckolodziej@anl.gov

DOE Technology Development Manager:
Kevin Stork

- Decouple the HoV effect from RON for additional fuel hydrocarbons from the down-selected Co-Optimization of Fuels & Engine (Co-Optima) list of 20 ■

Introduction

The CFR F1/F2 fuel octane rating engine is well-established for measuring fuel RON and Motoring Octane Number (MON). However, the actual cylinder conditions during RON measurement and their relation to fuel performance in production engines is not well understood. At the time that the ASTM RON and MON test protocols were established, all commercial fuels generally had the same HoV, so its effect on octane measurement was not a significant concern. This however has changed with the increased use of ethanol as an octane improver and renewable fuel component. The HoV of ethanol is approximately three times that of commercial gasoline blends [1]. So the effect of increased fuel HoV on RON measurement is unclear.

Previous research by Stein et al. has shown the advantages of increased RON from addition of ethanol [2]. However, work by Sluder et al. showed that HoV may not have a significant effect on combustion phasing under knock-limited spark advance conditions when RON and sensitivity (RON-MON) were kept constant and HoV varied [3]. Foong et al. used a CFR F1/F2 engine to try to separate the effect of increased HoV of fuels with ethanol splash blended, meaning HoV and RON increased at the same time [4]. To account for the cooling effect of the increased ethanol and HoV, the intake air temperature upstream of the carburetor was increased above the standard RON conditions so as to maintain intake port

temperature. As a result, the equivalent RON rating (with increased intake air temperature) of the increased ethanol content fuel blends was lower than the standard RON measurement. This showed that the increased HoV of the fuels inflated their actual RON rating. However, since the fuel HoV and RON increased at the same time, it was necessary to increase the engine compression ratio as RON increased. One of the objectives of this work was to see if similar results would be seen if the HoV increased with ethanol content, but the RON remained the same by reducing the PRF (octane rating) of the base blending fuel.

Approach

This project investigates the effect of fuel HoV on fuel auto-ignition characteristics and how that relates to a fuels’ octane rating. Fuel HoV, RON, and sensitivity are three key parameters in the Co-Optima fuels merit function. The goal is to better understand the standard RON test conditions and how HoV can affect that result. This is a combined approach, using CFR F1/F2 experimental testing and 1D modeling to characterize fuel effects on the engine combustion conditions. This information is fed into three-dimensional computational fluid dynamics simulations by collaborating with another Co-Optima project. With this increased knowledge, it will be possible to refine the importance of these fuel parameters in the Co-Optima merit function.

Results

Engine Instrumentation

A CFR F1/F2 engine was installed, instrumented, and commissioned at Argonne National Laboratory during the last fiscal year (Figure 1). Several modern engine combustion research devices have been installed on the engine to provide more information on the engine cylinder and operating conditions, without affecting the engine’s ability to run under ASTM standardized fuel octane rating tests. Some of these modifications include:

- AVL and LabVIEW data acquisition systems for high and low speed measurement signals
- Crankshaft encoder, spark current clamp, and spark plug cylinder pressure transducer for calculation of heat release, combustion noise, and knock
- Temperature and high speed pressure measurements in the intake and exhaust ports for 1D GT-POWER modeling
- Lambda sensor and emissions sampling probe installed in the exhaust system

- Engine has retained original combustion chamber geometry and knock meter pickup to continue ASTM RON and MON fuel octane testing

1D GT-POWER Model

A 1D GT-POWER engine model has been created to provide more details of the cylinder pressure and temperatures during testing. Three models of the CFR F1/F2 engine have been constructed in GT-POWER: RON, MON, and three-point analysis. The CFR F1/F2 configuration is shown in Figure 1 and the RON model can be seen in Figure 2. The MON model includes the CFR mixture heater between the exit of the carburetor and the engine intake port. The three-point analysis model is a simplified version of the RON and MON models that only requires the fluid boundary conditions at the intake and exhaust ports.

Investigation of RON Engine Conditions

Under the ASTM standard RON test, each fuel should be tested in the engine at the excess air ratio (λ) where it achieves maximum knocking conditions, as measured



Figure 1. Instrumented and commissioned CFR F1/F2 fuels rating test engine installed at Argonne National Laboratory

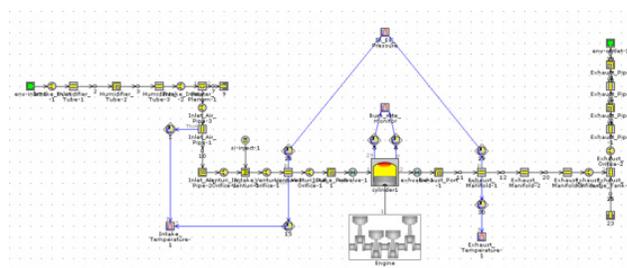


Figure 2. Schematic of the RON 1D GT-POWER model

by a knock meter. Lambda sweeps were performed to demonstrate the peak knocking lambda for PRF fuels from 90 to 100 octane number (PRF90 to PRF100), as shown in Figure 3. It was demonstrated that peak knocking lambda was consistently 0.90 ± 0.01 for all PRF fuels from PFR90 to PFR100.

Throughout the Co-Optima program, there is a high level of interest in a RON 98 fuel blend for its anti-knock qualities. This work focused on ethanol HoV testing for PRF-ethanol blends that had a constant RON of 98. To determine the appropriate pre-ethanol PRF octane level, several iterations were performed at each level of ethanol addition. The results of those blending studies are shown in Table 1. As the percent volume ethanol concentration increased, the associated octane level of the PRF blendstock decreased.

Once the PRF-ethanol blends were established for constant RON 98, lambda sweeps were performed to

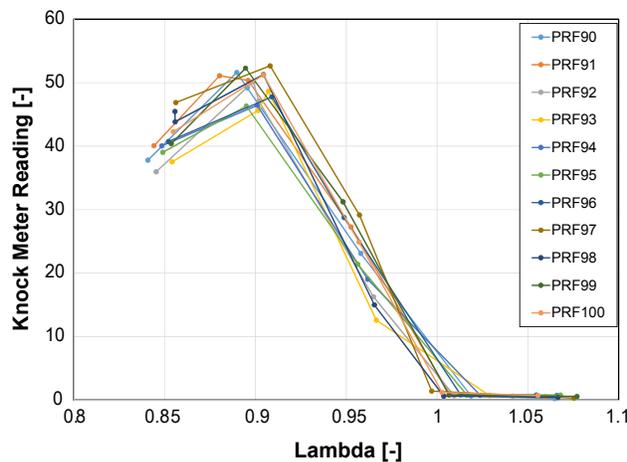


Figure 3. Peak knocking lambda for PRF90 to PRF100 fuels

Table 1. Required PRF Blendstock with Ethanol for RON 98 Fuel Blends

Ethanol (%)	RON (-)	PRF Blendstock (-)
0	98	98
10	98	90.2
20	98	81.5
30	98	70.5
40	98	57.5
50	98	40

determine each fuel blends' peak knocking lambda. Figure 4 shows the results of those PRF-ethanol lambda sweeps. The lambda of peak knock shifted from 0.9 for a pure PRF98 fuel (0% ethanol) to 0.95 for a 50% ethanol PRF fuel blend. The change in peak knocking lambda could mean differences in the characteristics of the end-gas in the combustion chamber where auto-ignition initiated, affecting the overrating or underrating of a fuel's octane number.

More detailed analysis revealed additional differences in the engine cylinder conditions and operating conditions as ethanol content increased in the 98 RON PRF-ethanol fuel blends. As observed by Foong et al., the mixture temperature, measured at the exit of the carburetor entering the intake port, was significantly lower as ethanol content and fuel HoV increased [4]. Foong et al. normalized for the cooling effect of the fuel blend's increasing HoV by increasing the intake air temperature upstream of the carburetor. Note that in Foong's work, this method was applied to splash-blended PRF-ethanol blends (meaning RON and therefore CFR compression ratio increased with ethanol addition), while in this study that method was applied to match-blended PRF-ethanol fuels (constant RON and compression ratio). Given that the RON method does not take the HoV of the fuel into account, the PRF-ethanol mixtures with constant 98 RON should show increased knocking as the intake air temperature increases.

Figure 5 shows the amount of change in RON that occurred for PRF-ethanol blends while heating the intake air temperature to normalize the mixture temperature back to that of standard conditions. The X-axis shows the relative increase in rate of HoV cooling based on

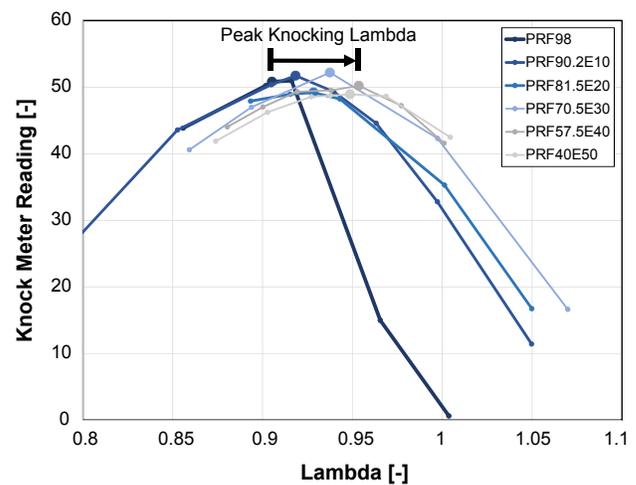


Figure 4. Peak knocking lambda for 0% to 50% PRF-ethanol blends with RON 98

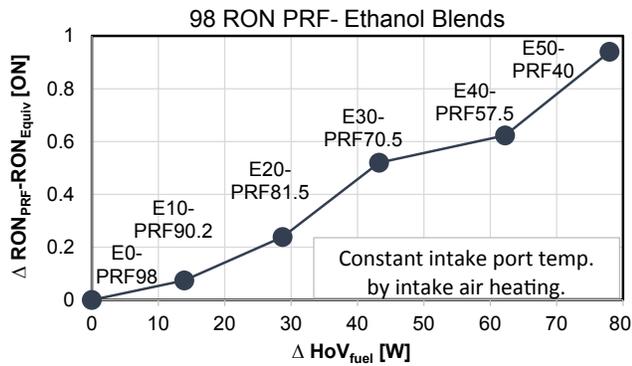


Figure 5. Knocking-derived octane number (ON) difference for PRF-ethanol blends between standard RON operating conditions and normalized mixture temperature RON equivalent

fuel HoV and fuel flow rate compared to standard PRF operation. At increasing levels of intake air heating as the ethanol content increased, the delta between standard RON knocking and knocking with the normalized mixture temperature increased. The increase in knocking can be used to calculate an “equivalent RON” of the fuel blend. By heating the intake air to normalize the mixture temperature under increased ethanol (and HoV) conditions, it is possible to determine the HoV contribution to the fuel blend’s RON rating. This means that the contribution of HoV to the octane rating of a 98 RON PRF-ethanol fuel blend with 30% ethanol exceeded 0.5 octane units, and with 50% ethanol by 1 octane unit.

However, the delta between standard RON knocking and equivalent RON knocking (under normalized mixture temperature conditions) was not the only difference noticed between the standard PRF octane rating fuels and the ethanol-blended test fuels. Figure 6 shows that the fuel energy rate entering the combustion chamber and the engine’s load was reduced as a result of both leaner lambdas for peak knock (see Figure 4) and the reduction of the fuel blend’s lower heating value (because ethanol’s lower heating value is significantly lower than the PRF mixture). So while the intake air temperature normalization method can determine the overestimation of RON for fuels with higher HoV, this work has found additional differences in engine cylinder and operating conditions which also affect the ASTM RON test protocol.

Conclusions

- By use of a newly commissioned and instrumented CFR F1/F2 engine, match-blended PRF-ethanol fuels were

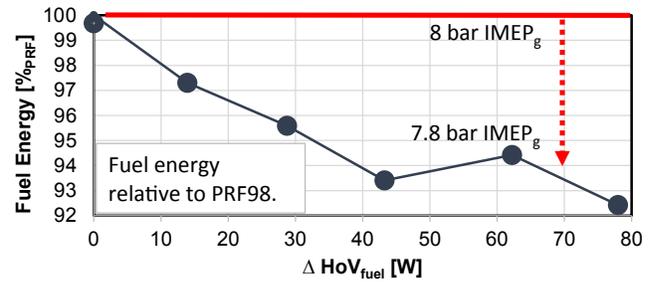


Figure 6. Reduction in fuel energy and engine indicated mean effective pressure (IMEP) for PRF-ethanol blends compared to standard PRF fuel operation

used in a mixture temperature normalization method to find the HoV contribution to RON rating.

- Among PRF90 to PRF100 fuels, the peak knocking lambda was at 0.9 ± 0.01 .
- When up to 50% ethanol is added to the fuel blend, peak knocking lambda shifted to 0.95 ± 0.01 , potentially affecting the reactivity of the cylinder end-gas.
- When mixture temperatures are normalized for higher HoV fuel blends (in this case with ethanol), the contribution to RON can exceed 0.5 octane units at 30% ethanol and 1 octane unit at 50% ethanol.
- While normalization of mixture temperature through intake air heating captured some of the HoV effect, these tests revealed that this method didn’t account for all differences between PRF and test fuels, and that in some ways new artifacts were introduced.

References

1. Heywood, J.B., “Internal Combustion Engine Fundamentals,” McGraw-Hill, New York, NY, 1988.
2. Stein, R., Polovina, D., Roth, K., Foster, M. et al., “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.
3. Sluder, C., Szybist, J., McCormick, R., Ratcliff, M. et al., “Exploring the Relationship Between Octane Sensitivity and Heat-of-Vaporization,” SAE Int. J. Fuels Lubr. 9(1):2016, doi:10.4271/2016-01-0836.
4. Foong, T. M., Morganti, K. J., Brear, M. J., da Silva, G., et al., “The Octane Numbers of Ethanol Blended with Gasoline and its Surrogates,” *Fuel* 115:727-739, 2014.

5. Anderson, J., Leone, T., Shelby, M., Wallington, T. et al., "Octane Numbers of Ethanol-Gasoline Blends: Measurements and Novel Estimation Method from Molar Composition," SAE Technical Paper 2012-01-1274, 2012, doi:10.4271/2012-01-1274.

II.3 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) 2016 Objectives

- Conduct engine-based studies and vehicle modeling to support the U.S. DRIVE Fuels Working Group's planned well-to-wheels study of high-octane fuels
- Contribute to Co-Optimization of Fuels & Engines project meetings and discussions

FY 2016 Accomplishments

- Procured fuels for U.S. DRIVE Fuels Working Group's Fuel Set B
- Completed engine studies of 97 Research Octane Number (RON) fuels in Fuel Set B
- Began studies of 101 RON fuels in Fuel Set B
- Led development and procurement of the Co-Optima "core" fuels matrix of 97 RON fuels

Future Directions

- Complete engine studies and vehicle modeling in support of the U.S. DRIVE Fuels Working Group's well-to-wheels study
- Evaluate candidate fuel blends generated by the Co-Optima project for potential efficiency improvement in the Ford 1.6 L engine and in vehicle models ■

Introduction

Engine downsizing is an important facet of increasing vehicle fuel efficiency while maintaining performance at a level that customers demand. As the original equipment manufacturers 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.

Scott Sluder

Oak Ridge National Laboratory (ORNL)
2360 Cherahala Blvd.
Knoxville, TN 37932
Phone: (865) 946-1235
Email: sluders@ornl.gov

DOE Technology Development Manager:
Kevin Stork

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 heat of vaporization 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-grade 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

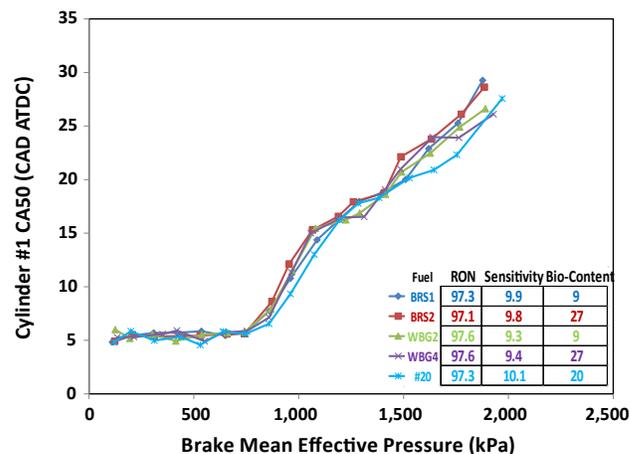
ORNL will investigate the potential fuel economy impacts of the use of higher-octane gasoline blends. At least three pathways for octane increase will be investigated. These paths include the use of ethanol, butanol, and a high-octane hydrocarbon blend. ORNL is partnering with Ford Motor Company and making 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 downsized 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. Additionally, 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 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

The U.S. DRIVE Fuels Working Group defined a series of biofuels for inclusion in a well-to-wheels study of the potential benefits of increasing gasoline octane rating. The matrix of fuels includes two fuels that are blends containing 20% ethanol (E20) and six non-ethanol biofuel blends. This selection of fuels is intended to augment the ongoing Coordinating Research Council Advanced Vehicle/Fuel/Lubricants-20 study. The final fuel economy results from Advanced Vehicle/Fuel/Lubricants-20 and Fuel Set B will be investigated to examine the CO₂ production and energy use predicted for production of these high-octane blends, with a goal of determining

potentially high-value directions for achieving an overall reduction in energy use in the transportation sector. The non-ethanol biofuels are blends of a woody-biomass-derived gasoline and blends that include a surrogate blending stream that is intended to approximate the formulation of bio-derived reformat streams. Engine-based studies of the 97 RON blends in this matrix were completed and vehicle modeling initiated. An engine failure prevented study of the 101 RON fuels in FY 2016, but these results are anticipated in the first half of FY 2017.

Figure 1 shows the location of 50% burn (CA50) for the 97 RON fuels, including results for the bio-reformat surrogate (BRS) fuels, the wood-based biogasoline (WBG) fuels, and an E20 blend (#20). These data were collected using pistons that produced a compression ratio of 11.4. At low brake mean effective pressure (BMEP), the combustion phasing is not limited by knock. As BMEP increases, combustion phasing is retarded to avoid the onset of knock. The RON and sensitivity results for these fuels showed that they were well-matched in terms of anti-knock performance, despite a wide span in the amount of bio-derived material in the fuels. The E20 fuel exhibits an advantage in combustion phasing at high BMEP levels, but otherwise these fuels exhibit similar performance, as might be expected from their well-matched RON and sensitivity values. Fuel mean effective pressure results also indicate good agreement between the fuels. These results are shown in Figure 2. Fuel mean effective pressure is a measure of the fuel energy used per engine cycle, normalized by the displacement of the engine. The data demonstrate good repeatability in the engine test cell as well as good agreement in the



CAD – crank angle degrees; ATDC – after top dead center

Figure 1. 2,000 rpm CA50 results for the 97 RON fuels at compression ratio 11.4

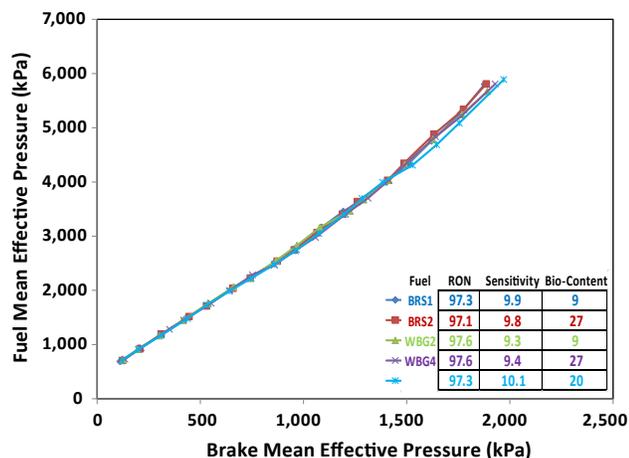


Figure 2. 2,000 rpm fuel mean effective results for the 97 RON fuels at a compression ratio of 11.4

determination of the net heating value for all of the fuels. Data were collected at engine speeds of 1,000 rpm, 1,500 rpm, 2,000 rpm, 2,500 rpm, and 5,000 rpm. These data are currently being used to model the fuel economy of both a mid-size sedan and a small sport utility vehicle, with results expect in early FY 2017.

An effort was made within the Co-Optimization of Fuels & Engines program to identify a set of core fuels to underpin studies of octane rating, sensitivity, and heat of vaporization within the advanced engine development team. Staff at ORNL led development and later acquisition of these fuels. Three fuels were initially sought, with matching RON of approximately 98. The first fuel desired was a fuel composed mainly of saturates and having a sensitivity of nearly zero. The second fuel was a 30% ethanol blend, with sensitivity in excess of 10. Finally, a high-aromatic fuel was desired that would match the sensitivity of the 30% ethanol blend, but sourcing the sensitivity from aromatic compounds. Linear blends of these three fuels then enables studies of sensitivity and heat of vaporization effects at approximately constant RON. The relationship among these fuel properties is one of intense interest. ORNL contracted with Gage Products of Ferndale, Michigan, to produce the fuels on behalf of the interested researchers within the Co-Optima project. The fuels were procured in FY 2016 and shipped to each interested lab for experimental studies.

Conclusions

- Fuel Set B results to date show similar performance for fuels with well-matched RON and sensitivity. Vehicle fuel economy results derived from the engine studies of these fuels are forthcoming.
- Co-Optima core fuels were formulated at 98 RON to enable investigation of the effects of heat of vaporization and sensitivity. Results of study of these fuels are expected in FY 2017.

References

1. Robert A. Stein, Dusan Polovina, Kevin Roth, Michael Fost, Michael Lynskey, Todd Whiting, 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.

II.4 Alternative Fuels DISI Engine Research – Stratified Lean and Homogeneous Lean

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 the most efficient use of future fuels

Fiscal Year (FY) 2016 Objectives

- Continue 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
- Enhance stratified charge operation by developing effective double-injection strategies and combine with intake boost
- Identify in-cylinder mechanisms that affect the stability of ultra-lean well-mixed lean SI operation
- Develop a partial fuel stratification technique further to allow the use of a smaller amount of fuel near the spark plug

FY 2016 Accomplishments

- Continued examination of effects of fuel blends on stratified operation at various speeds and intake pressures; refined double-injection strategies, as guided by high-speed imaging of liquid fuel, measured combustion stability, and measured smoke emissions
- Demonstrated infrared (IR) detection of vapor penetration of E85 (85% ethanol, 15% gasoline blend by volume) and gasoline fuel sprays; used high-speed particle image velocimetry (PIV), IR, and flame imaging to reveal tumble-induced asymmetry of fuel vapor which causes elevated soot emissions at 2,000 rpm
- Investigated three Co-Optima Core Fuels for boosted stratified charge operation at 2,000 rpm; showed strong effect of fuel composition on smoke emissions
- Used optical techniques to refine partial fuel stratification technique to allow the use of a smaller

Magnus Sjöberg (Primary Contact), Wei Zeng, David Vuilleumier

Sandia National Laboratories
MS9053, PO Box 969
Livermore, CA 94551-0969
Phone: (925) 294-3635
Email: mgsjobe@sandia.gov

DOE Technology Development Manager:
Kevin Stork

pilot fuel quantity while maintaining stable ultra-lean SI combustion with an E30 (30% ethanol, 70% gasoline blend by volume) fuel

- Used PIV to measure effects of flow field on early flame development for well-mixed ultra-lean SI operation with E30; identified flow conditions that support stable combustion
- Packaged PIV, flow, and boundary conditions data, including a GT-POWER model, and transferred to computational fluid dynamics (CFD) modelers at Argonne National Laboratory
- Addressed one of the barriers identified by DOE Vehicle Technologies Office: inadequate data for fuel property effects on combustion and engine efficiency optimization

Future Directions

- Continue to further the scientific understanding of advanced and efficient combustion modes, using blends of gasoline, ethanol, and new biofuels in an optical DISI engine
- Incorporate new fuel components and blends in coordination with other Co-Optima tasks
- Expand conceptual model of swirl-spray stabilization mechanism to include double injections of E0-E30 fuels for boosted stratified operation
- Examine how the dominant soot production pathway of stratified charge combustion changes with operating conditions and fuel composition

- Investigate experimentally lean or dilute well-mixed mixed-mode SI combustion, with a focus on combustion stability and peak apparent heat release rate
- Support CFD and chemical kinetics modeling groups by providing validation data for in-cylinder flows, deflagration, and end-gas autoignition ■

Introduction

Ever tighter fuel economy standards and concerns about global climate change motivate efforts to improve engine efficiency and to develop 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. Here, the 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, the focus is on techniques that can overcome these challenges. Specifically, fuel stratification is used to ensure ignition and completeness of combustion but this technique 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 for fast combustion. However, such mixed-mode combustion requires very stable inflammation, motivating studies on the effects of near-spark flow and turbulence.

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 wide ranges of operating conditions and alternative fuel blends. Second, in-cylinder processes are examined with high-speed optical diagnostics, including advanced laser-based techniques. Computer modeling 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 sections, examples of accomplishments during FY 2016 are presented.

Stratified-Charge Operation

Figure 1 shows a cross-section of the stratified charge capable combustion system of the SI engine used here. Only three out of eight fuel sprays are shown in this illustration. The injector is oriented such that two of the sprays straddle the spark plug gap. For stable and clean combustion, the interaction of the fuel sprays and the intake-generated flow is important. Specifically, the use of intake-generated swirl can stabilize stratified charge combustion, avoiding the appearance of occasional partial burns or misfires [1]. The interaction of the eight fuel sprays with the swirling gas flow stabilizes the flow at the time and location of the spark, as described in Zeng et al. [1,2]. In this hardware configuration, the swirling flow is generated by deactivating one intake valve. Flow bench measurements reveal that operation with one valve increases the strength of the tumble flow as well. At the same time, emissions measurements show that smoke levels can become unacceptably high when the engine speed is increased from 1,000 to 2,000 rpm. To investigate the cause of the elevated smoke, multiple optical diagnostics techniques were applied, as described in Zeng et al. [3]. High-speed IR fuel-vapor detection was of particular utility for understanding the elevated smoke emissions. This technique was developed at Sandia by Hecht et al. [4]. By applying a band-pass filter centered at $3.20 \mu\text{m} \pm 300 \text{ nm}$, thermal emission from the C-H stretch band near a wavelength of $3.4 \mu\text{m}$ can be detected. This band is well isolated from most other emitting species, in particular H_2O and CO_2 . A FLIR SC6800 camera was used for these tests, and Figure 2a shows one example of fuel vapor jet detection during the injection event. Overlaid are liquid contours detected with another camera

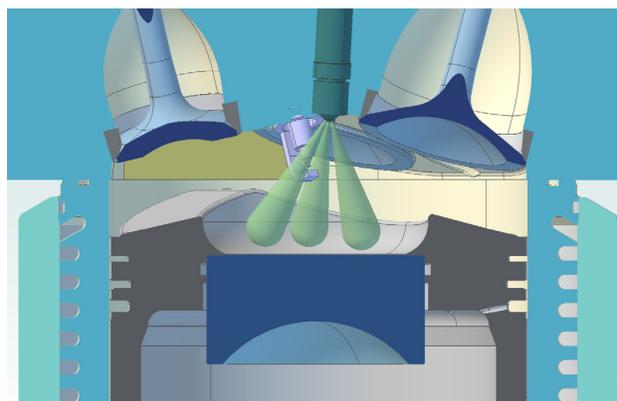


Figure 1. Cross-section of combustion chamber at -35° crank angle (CA) after top dead center for the spray-guided stratified charge DISI engine used here. A piston bowl window with a concave surface provides a wide-angle view into the combustion chamber.

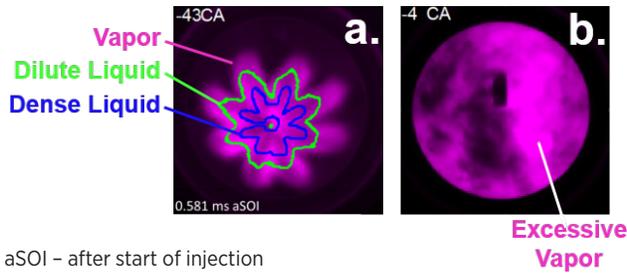
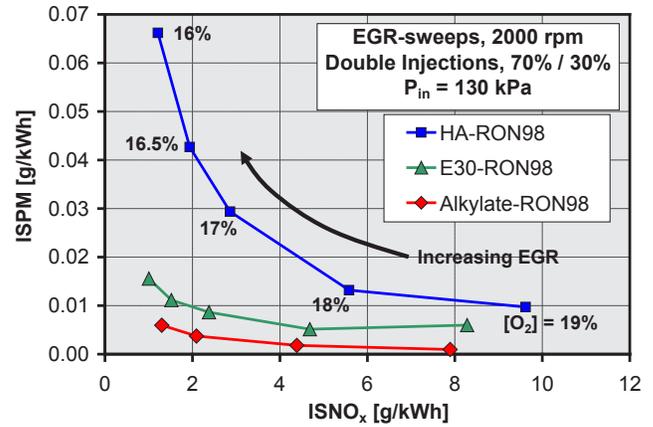


Figure 2. (a) Detection of gasoline vapor jets beyond liquid fuel penetration during fuel injection. (b) Identification of excessive vapor concentration near top dead center due to tumble-induced vapor asymmetry for stratified charge operation at 2,000 rpm.

using a Mie-scattering technique. Already during the fuel injection event, effects of the combined swirl–tumble flow can be seen on the penetrating fuel vapor jets. After the fuel injection, the fuel jet structures disappear and the fuel vapor motion gradually becomes dominated by the intake-generated flow. Approaching top dead center, Figure 2b shows that a clear vapor asymmetry has developed with more fuel on the right-hand side of the piston bowl. Flame imaging reveal strong soot luminosity from this area, which indicates that the elevated smoke stems from this tumble-induced fuel vapor asymmetry. In contrast, for operation with two intake valves, the fuel vapor distribution remains symmetric [3].

These results highlight a drawback of the current approach to generate in-cylinder swirl for stabilization of stratified charge combustion. For future hardware development, it may be beneficial to reconfigure the intake ports to generate the required swirl while minimizing the tumble components of the flow. Even so, it is not likely that all flow-induced imperfections in the vapor–fuel distribution can be avoided. Therefore, it is valuable to learn how to operate the engine such that smoke generation is minimized even for the current combustion system that tends to create fuel vapor asymmetry at elevated engine speed. In the context of alternative fuels research, it is also important to consider the sooting propensity of the fuel being developed. Consequently, three Co-Optima Core Fuels were investigated. Figure 3 shows the trade-offs between smoke and NO_x for stratified charge operation with intake boost and double injections at 2,000 rpm. For all three fuels, smoke generally increases when increasing amounts of exhaust gas recirculation are used to suppress NO_x . However, for a given NO_x level, the smoke level varies widely between the three fuels. The high-aromatic (HA) fuel stands out with the highest smoke level, which is consistent with expectations based on fuel composition.



RON – Research Octane Number; ISPM – indicated specific particulate matter; ISNO_x – indicated specific NO_x

Figure 3. NO_x –soot trade-offs when exhaust gas recirculation (EGR) is applied to boosted stratified charge operation at 2,000 rpm using three Co-Optima Core Fuels

The high-aromatics and E30 fuels have comparable distillation characteristics, see Table 1, and here the benefit of the oxygenated ethanol content is clear. The alkylate fuel contains solely saturated hydrocarbons (i.e., paraffins), and it also has a low final boiling point. These fuel properties win over the moderate oxygen content of the E30 fuel, so the alkylate fuel shows superiorly low smoke emissions.

Lean Well-Mixed Operation

Lean or dilute well-mixed SI engine operation can improve thermal efficiency, but one key challenge is to maintain stable combustion without misfires. Another challenge is to maintain a 10–90% burn duration below

Table 1. Selected Fuel Properties and Ratings for the Three Co-Optima Core Fuels Used in the Study Presented in Figure 3

	<i>Alkylate</i>	<i>E30</i>	<i>High Aromatic</i>
RON	98	98	98
MON	97	88	87
T10 (°C)	93	61	59
T50 (°C)	100	74	108
T90 (°C)	106	155	158
TF (°C)	161	204	204
Aromatics (Vol. %)	0	8	31
Olefins (Vol. %)	0	5	4
Paraffins (Vol. %)	100	57	65
Ethanol (Vol. %)	0	30	0

MON – Motor Octane Number; TF – final boiling point; T10 – temperature for 10% distilled; T50 – temperature for 50% distilled; T90 – temperature for 90% distilled

30°C [5,6]. The latter can be achieved via the use of mixed-mode combustion, which features a combination of turbulent deflagration and end-gas autoignition [6], which rapidly completes combustion. For engine development, it is important that CFD models can handle well both lean ignition and mixed-mode combustion. Current optical engine research supports these challenges. Figure 4 provides an example of PIV imaging of lean well-mixed SI engine operation with $\phi = 0.55$, using an E30 fuel. In addition to enabling laser-based measurements of the flow field, the silicon-oil droplets vaporize in the flame front, allowing the flame front to be tracked as it develops from the spark plug location. To identify combinations of flow strength and direction that benefit this type of ultra-lean operation, extensive data sets of high-speed PIV data were processed statistically. Figure 5 provides one example of the results. The data processing reveals that in order to generate strong flame development that leads to beneficial mixed-mode combustion, fairly high flow speeds near the spark plug should be combined with a flow angle of less than 210°, as defined in Figure 4. On the contrary, weak combustion is most likely to occur on cycles that feature weak flow near the spark plug in combination with flow angles greater than 210°. These observations in combination with CFD modeling can potentially elucidate the fundamentals of how to achieve robust flame development for ultra-lean SI combustion. Hence, extensive validation data sets like these have

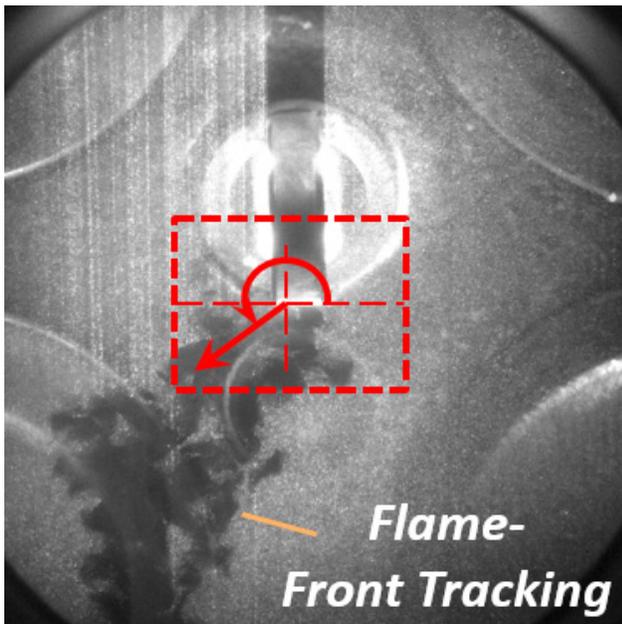


Figure 4. The use of high-speed PIV for tracking of flow field and flame wrinkling, here for ultra-lean SI operation with $\phi = 0.55$ and E30 fuel

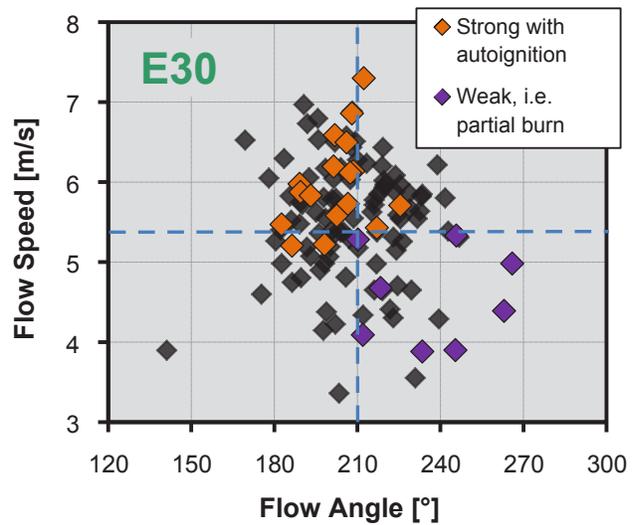


Figure 5. Flow strength plotted against flow direction during early flame development for 105 cycles, with identification of either weak partial burns or strong cycles with autoignition for mixed-mode combustion. Ultra-lean SI operation with $\phi = 0.55$ and E30 fuel.

been transferred to CFD modelers at Argonne National Laboratory, who are using both Reynolds-average Navier–Stokes- and large eddy simulation-type models.

Conclusions

- The Alternative Fuels DISI Engine Lab at Sandia contributes to the science base needed by industry to take full advantage of future fuels while advancing the state-of-the-art for SI engine combustion.
- Intake-generated swirl stabilizes combustion for the current hardware configuration for stratified charge SI operation. However, the associated increase of tumble causes an asymmetry of the fuel vapor, which correlates with increased engine-out smoke at elevated engine speeds.
- The three Co-Optima Core Fuels show vastly different tendencies to form smoke at an engine speed of 2,000 rpm, with the high-aromatic fuel performing worst.
- The interaction of the intake-generated flow and the early flame is very important to achieve stable ultra-lean well-mixed operation. High-speed flow, plasma and flame imaging reveals that certain combinations of flow strength and direction are favorable for fast inflammation.

References

1. 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,” *International Journal of Engine Research*, 16(3):306–322, 2014.
2. 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,” *Combustion and Flame* 168:166–185, 2016, doi: 10.1016/j.combustflame.2016.03.015.
3. W. Zeng, M. Sjöberg, D.L. Reuss, and Z. Hu, “High-Speed PIV, Spray, Combustion Luminosity, and Infrared Fuel-Vapor Imaging for Probing Tumble-Flow-Induced Asymmetry of Gasoline Distribution in a Spray-Guided Stratified-Charge DISI Engine,” *Proceedings of the Combustion Institute*, 2016, doi: 10.1016/j.proci.2016.08.047.
4. W.E. Eagle, L. Malbec, and M.P.B. Musculus, “Comparing Vapor Penetration Measurements from IR Thermography of C-H Stretch with Schlieren during Fuel Injection in a Heavy-Duty Diesel Engine,” 9th U.S. National Combustion Meeting, 2015.
5. F. Ayala and J. Heywood, “Lean SI Engines: The role of combustion variability in defining lean limits,” *SAE Technical Paper 2007-24-0030*, 2007, doi:10.4271/2007-24-0030.
6. 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,” *SAE Int. J. Engines* 9(2):750–767, 2016, doi:10.4271/2016-01-0689.
3. W. Zeng, M. Sjöberg, D.L. Reuss, and Z. Hu, “High-Speed PIV, Spray, Flame and Infrared Fuel-Vapor Imaging for Probing Tumble-Flow-Induced Asymmetry of Gasoline Distribution in a Spray-Guided Stratified-Charge DISI Engine,” presented at AEC Program Review Meeting at Sandia, February 2016.
4. W. Zeng, M. Sjöberg, D.L. Reuss, and Z. Hu, “High-Speed PIV, Spray, Combustion Luminosity, and Infrared Fuel-Vapor Imaging for Probing Tumble-Flow-Induced Asymmetry of Gasoline Distribution in a Spray-Guided Stratified-Charge DISI Engine,” presented at 36th International Symposium on Combustion and published in the *Proceedings of the Combustion Institute*, 2016.
5. W. Zeng and M. Sjöberg, “Utilizing Boost and Double Injections for Enhanced Stratified-Charge DISI Operation with Gasoline and E30 Fuels,” presented and published at THIESEL 2016.

Special Recognitions and Awards/ Patents Issued

1. 2015 U.S. DRIVE Highlight: “Mechanism for Stabilizing Fuel-Efficient, Stratified SI Operation Identified.”

Acknowledgements

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

FY 2016 Publications/Presentations

1. J. Szybist et al., Co-Optima presentation to DOE EERE, “Understanding Octane Number and its Relevance to Modern and Emerging Engines,” September 2015.
2. 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,” *Combustion and Flame*, 2016.

II.5 Fuel Effects on EGR and Lean Dilution Limits on SI Combustion

Overall Objectives

- Verify the Co-Optimization of Fuels & Engines (Co-Optima) “Central Fuel Hypothesis” assumption that fuel laminar flame speed (LFS) can describe the limits of exhaust gas recirculation (EGR) and lean dilute spark ignition (SI) combustion
- Quantify the relative impact of fuel properties on dilution tolerance compared to engine design parameters

Fiscal Year (FY) 2016 Objectives

- Evaluate hypothesis that fuel LFS at nominal conditions can be used to predict EGR and lean dilution tolerance in an SI engine
- Create and execute a test campaign with a fuels test matrix using pure components that normalizes for fuel heat of vaporization (HoV) differences
- Compare the effects of fuel properties to engine design parameters (tumble, ignition energy, and injection location) on extending EGR and lean dilution limits

FY 2016 Accomplishments

- Determined that among alcohol blended fuels, increased fuel LFS and HoV allowed for 4–6% increased EGR dilution and some lean tolerance increase (0.05–0.1 higher lambda), providing approximately 1–2% higher engine indicated thermal efficiency (ITE)
- Quantified that increased cylinder charge motion, either by tumble or direct injection, increased EGR dilution tolerance by 2% and lean limits by 0.1 lambda, providing approximately 1% higher engine ITE
- Demonstrated that fuel LFS and HoV can have as big of an effect, if not larger, on engine EGR dilution limits and increased ITE than only changes to engine design parameters
- Ascertained that under lean conditions, engine design parameters that affect cylinder charge motion had a much larger effect on lean operating limits compared to fuel LFS and HoV changes

Christopher P. Kolodziej (Primary Contact), Thomas Wallner, James Sevik, Michael Pamminger

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
Phone: (630) 252-1599
Email: ckolodziej@anl.gov

DOE Technology Development Manager:
Kevin Stork

Future Directions

- Expand experiments on the positive effects of fuel LFS and HoV for alcohol fuel blends, by comparing with other families of hydrocarbons
- Combine chemical kinetic modeling with experiments to estimate combustion flame speeds at engine relevant conditions
- Test fuels from the Co-Optima down-selected list of 20 components of interest ■

Introduction

Gasoline SI engines continue to dominate the U.S. passenger car fleet, and given the large amount of fuel consumed by this group of transportation, it is important to improve engine efficiency and reduce fuel consumption. One method of increased SI engine efficiency is through dilute combustion, either with EGR or by operating the engine lean (excess air) [1]. In both forms of dilute SI operation, engine ITE is increased by lower throttling and pumping losses, reduced heat transfer losses from the hot combustion gases to the cooler combustion chamber surfaces, and increased work extraction during the engine expansion stroke through a higher ratio of specific heats of the working fluid [2]. While engine efficiency increases with both EGR and lean dilution, the amount of dilution is limited by combustion stability.

Previous research has shown that the EGR or lean dilution limit of SI engine combustion may be extended both by fuel properties (LFS) or by engine design

characteristics [3]. Szybist and Splitter observed that increased EGR dilution tolerance was achieved by fuels of higher LFS with shorter flame development angle, the time from spark to start of combustion [4]. When ethanol was used to increase fuel LFS, increased EGR dilution tolerance was observed despite increased cylinder charge cooling due to higher fuel HoV. In this project, a unique fuels test matrix was designed to normalize the effects of fuel LFS and HoV by blending five pure component fuels at high LFS and low LFS levels. The effects of high and low fuel LFS on extended EGR and lean dilution limits were compared to engine design parameters.

Approach

This project investigates the impact of fuel laminar flame speed on efficient engine operation, as a key term in the Co-Optima fuels merit function. A fuel matrix was designed based on fuel LFS at nominal conditions, while normalizing for fuel HoV, with the help of chemical kinetic modeling from Lawrence Livermore National Laboratory. At the end, comparisons could be made for the relative effects of fuel LFS and engine design parameters on combustion EGR and lean dilution limits and engine efficiency.

Results

Testing was performed on a single-cylinder research engine with five fuels blends that had low LFS and HoV (Fuels 1–3) and high LFS and HoV (Fuels 4 and 5). The fuel blend matrix is shown in Figure 1. Engine design parameters, such as tumble, ignition energy, and direct or port fuel injection were also studied for each fuel. Each fuel was operated with increasing EGR dilution until the combustion became unstable (3% and 5% coefficient of variance [COV] of indicated mean effective pressure [IMEP]). In the same manner, each fuel was tested with increasingly lean air–fuel ratios until the combustion stability deteriorated. Each combination of fuel and engine operating parameters were tested in both EGR and lean dilution studies.

Effects of Fuel Properties

Each fuel blend was tested under both EGR and lean dilution sweeps until combustion stability deteriorated to 3% and 5% COV of IMEP. Figure 2 shows the EGR dilution limit for each fuel at a fixed level combustion stability of 3% COV of IMEP. The higher LFS fuels (Fuels 4 and 5) were able to achieve 4–6% higher EGR dilution, which allowed for 1–2% increased engine ITE.

Interestingly, there was not a significant difference in lean dilution limits between low and high LFS fuels at the

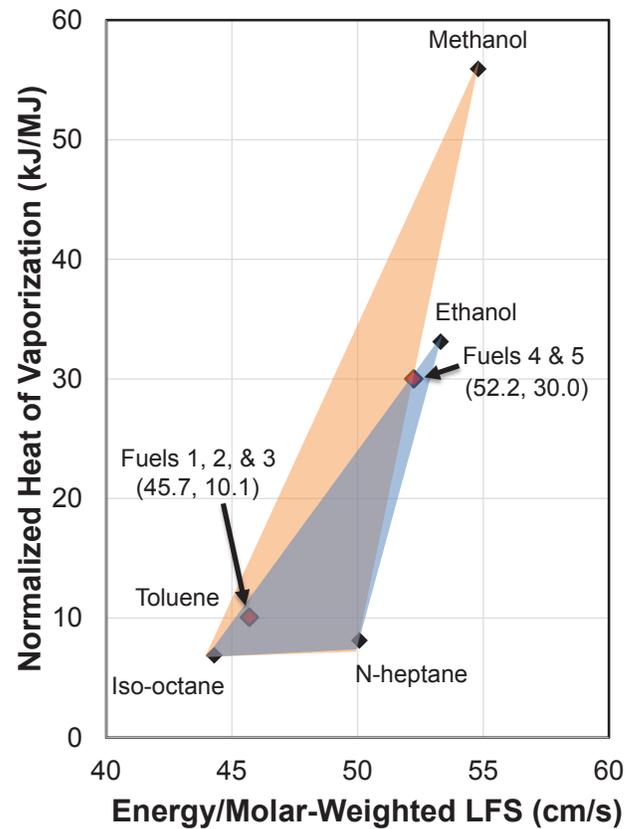


Figure 1. Graphical representation of fuel blending

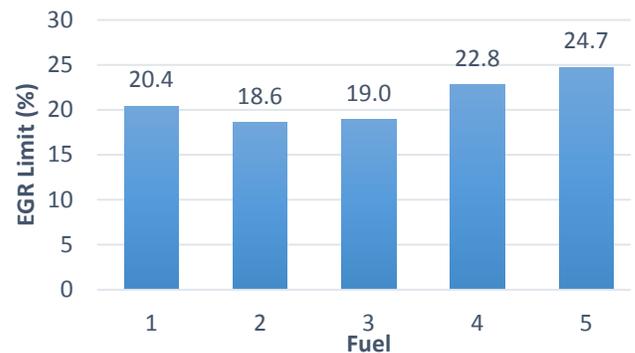


Figure 2. The EGR dilution tolerance at 3% COV of IMEP between all fuel blends

extent of normal combustion stability limits (3% COV of IMEP). It was not until the engine was operated leaner, and at an even less stable 5% COV of IMEP, that some trends were noticed between low and high LFS fuels. Figure 3 shows there was approximately a 0.1 lambda advantage for alcohol fuel blends with high LFS (Fuels 4 and 5) compared to the lower LFS alcohol fuel blends (Fuels 2 and 3). However, it also appeared that the low

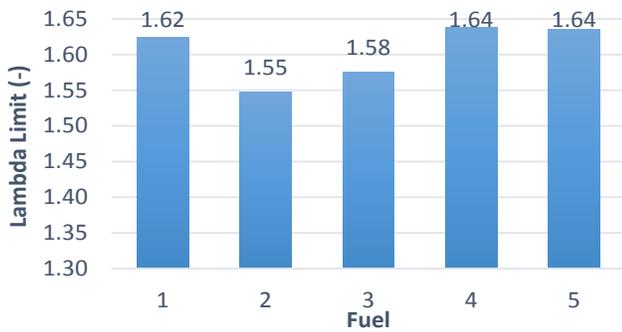


Figure 3. Lean tolerance of each fuel blend at 5% COV of IMEP

LFS aromatic fuel (Fuel 1) performed nearly as well as the higher LFS alcohol fuels (Fuels 4 and 5) at these less stable combustion conditions. This is motivation to further investigate differences in EGR and lean dilution performance between families of hydrocarbons.

Effects of Engine Design Parameters

The impact of engine design parameters was tested for representative low (Fuel 2) and high LFS (Fuel 4) fuel blends. These two fuels were chosen because they were both based on ethanol blends. Focusing on the results from the higher LFS Fuel 4, Figure 4 shows the EGR dilution tolerance for each combination of high tumble (HT), low tumble (LT), high ignition energy (HIE) and low ignition energy (LIE). High tumble allowed for approximately 2% higher EGR dilution tolerance, while higher ignition energy allowed for approximately 0.5–1% higher EGR dilution. Increased EGR dilution from more cylinder charge motion caused by the higher tumble provided approximately a 1% ITE advantage, however the effects of ignition energy on ITE were within the uncertainty of the measurement. Increased cylinder charge motion from direct injection versus port fuel injection also allowed for an additional approximately 2% increase in EGR dilution tolerance, and consequently an additional approximately 1% gain in engine ITE.

Under lean conditions (Figure 5), engine design parameters already had a noticeable effect at 3% COV of IMEP. Recall that to see differences in lean dilution tolerance between fuel blends, the combustion stability had to be deteriorated to 5% COV of IMEP. Higher tumble provided approximately a 0.1 lambda advantage in lean dilution limit, which provided approximately a 1% engine ITE increase. Under lean conditions, there was not a significant advantage of increased ignition energy. All of these observations were consistent between engine design parameters at less stable combustion, with 5% COV of IMEP.

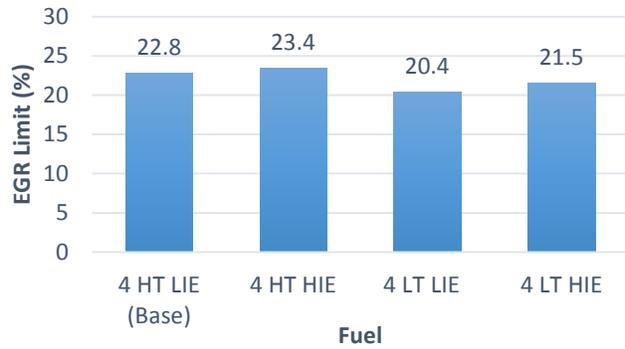


Figure 4. Comparison of engine design parameters on EGR dilution tolerance for Fuel 4 at 3% COV of IMEP

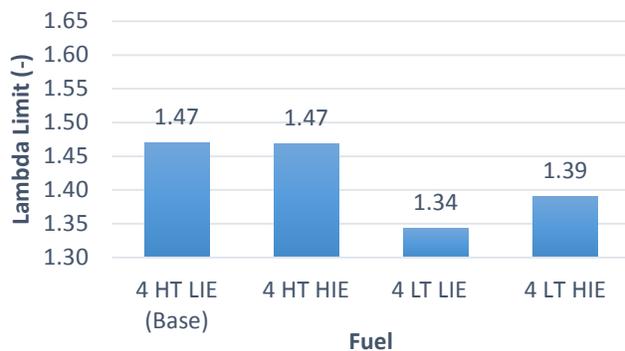


Figure 5. Comparison of engine design parameters on lean tolerance for Fuel 4 at 3% COV of IMEP

Combined Fuel and Engine Effects

In general, the effects of fuel LFS (and HoV) and engine design parameters on engine efficiency (ITE) can be summarized in Figure 6. Starting from a low LFS (and HoV) fuel at stoichiometric operation with no EGR, engine efficiency can be significantly increased by incorporating both a high LFS fuel and increased cylinder charge motion through higher tumble. At 1,500 rpm engine speed and 5.6 bar IMEP (common engine operating point in a vehicle), engine efficiency could potentially increase by as much as four percentage points under EGR dilution operation (to approximately 40% ITE) and as much as five percentage points under lean operation (to 41% ITE). This equates to significant improvements in vehicle fuel economy. Although lean operation allows higher engine efficiency, EGR dilute operation is currently the common approach used by vehicle manufacturers because emissions control can be performed with a three-way catalyst, which is less complex than a lean aftertreatment system.

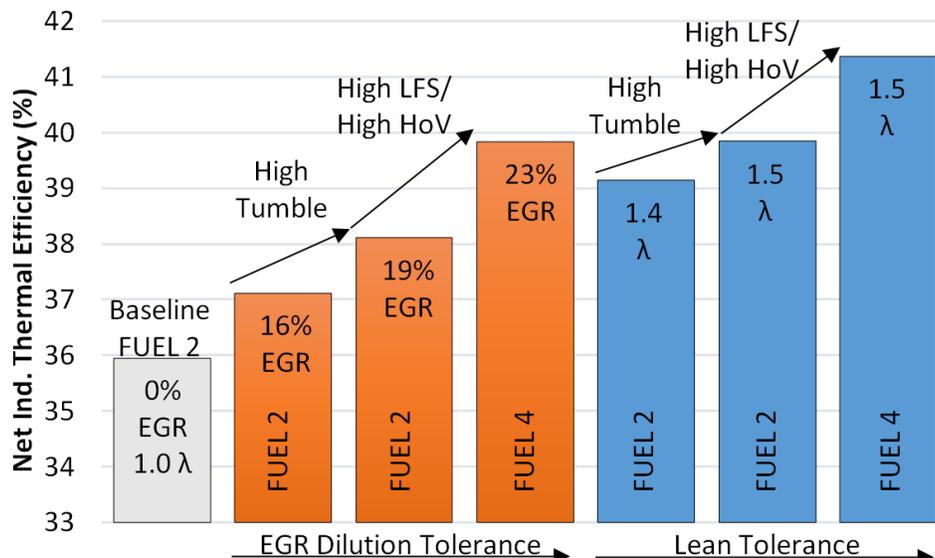


Figure 6. Overview of EGR dilution and lean operation effects on increased engine efficiency with the assistance of increased tumble and fuel laminar flame speed

Conclusions

Fuel LFS was determined to be an important fuel characteristic for future EGR and lean dilute SI engines for increased engine efficiency and reduced fuel consumption.

- A 4–6% increased EGR dilution limit and 0.05–0.1 higher lambda lean dilution limit allowed for an additional 1–2% increased engine thermodynamic efficiency for alcohol blended fuels, due only to fuel effects.
- EGR dilution tolerance was increased by 2% and lean dilution limits by 0.1 lambda through improvements to cylinder charge motion, providing an additional 1% higher engine thermodynamic efficiency, only through changes to engine design parameters.
- The impact of fuel LFS needs to be better defined for a wider range of hydrocarbon classes in how they affect engine efficiency in both EGR and lean dilute conditions.

References

1. Caton, J., “A Comparison of Lean Operation and Exhaust Gas Recirculation: Thermodynamic Reasons for the Increases of Efficiency,” SAE Technical Paper 2013-01-0266, 2013, doi:10.4271/2013-01-0266.
2. Heywood, J.B., “Internal Combustion Engine Fundamentals,” McGraw-Hill, New York, NY, 1988. p. 406–412.

3. Ozdor, N., Dulger, M., and Sher, E., “Cyclic Variability in Spark Ignition Engines A Literature Survey,” SAE Technical Paper 940987, 1994, doi:10.4271/940987.
4. Szybist, J. and Splitter, D., “Effects of Fuel Composition on EGR Dilution Tolerance in Spark Ignited Engines,” SAE Int. J. Engines 9(2):2016, doi:10.4271/2016-01-0715.

FY 2016 Publications/Presentations

1. Kolodziej, C.P., Pamminger, M., Sevik, J., Wallner, T., Wagnon, S.W., Pitz, W.J., “Fuel Effects on EGR and Lean Dilution Limits on SI Combustion,” presented to Co-Optimization of Fuels and Engines Advanced Engine Development and Fuels Properties teams, August 22, 2016.
2. Kolodziej, C.P., Pamminger, M., Sevik, J., Wallner, T., Wagnon, S.W., Pitz, W.J., “Effects of Fuel Laminar Flame Speed Compared to Engine Tumble Ratio, Ignition Energy, and Injection Strategy on Lean and EGR Dilute Spark Ignition Combustion,” SAE Technical Paper, April, 2017 (Draft submitted, in review.)

Special Recognitions and Awards/Patents Issued

1. Selected as one of the Co-Optimization of Fuels & Engines End of Year highlights for FY 2016.

II.6 Co-Optima: Gasoline-Like Fuel Effects at High Load

Overall Objectives

- The overall objective of the Co-Optimization of Fuels & Engines Initiative (Co-Optima) is to cooperatively develop emerging biofuels and advanced engine to bring these technologies to the market sooner to realize a reduction in petroleum consumption.
- This project aims to investigate the validity of the Co-Optima central fuel hypothesis, which states that a fuel candidate should perform in a manner commensurate with its properties regardless of its chemistry.
- Specifically, this project is investigating the knock propensity of fuels under boosted operating conditions for stoichiometric spark-ignited (SI) engines. Efforts in fiscal year (FY) 2016 were focused on non-dilute operation, and continuing work in FY 2017 will focus on exhaust gas recirculation (EGR) dilution.

FY 2016 Objectives

- Identify fuel-specific knock behavior under boosted operation that is not directly predicted by the Research Octane Number (RON) or Motor Octane Number (MON) in a stoichiometric SI engine
- Perform kinetic simulations to identify the underlying chemical reasons for the differences in the autoignition and knock behavior

FY 2016 Accomplishments

- Identified the occurrence of pre-spark heat release (PSHR) in a stoichiometric SI engine and its dependence on fuel composition
- Modeled the PSHR phenomenon successfully using detailed chemical kinetics, for three different fuels, verifying that PSHR tendency decreases as octane sensitivity (S) increases
- Identified that PSHR leads to a flame speed decrease for the main combustion event

Future Directions

- Evaluate up to eight fuels in FY 2017 under boosted conditions in a stoichiometric engine, including the Co-Optima core fuel matrix and three Co-Optima biofuel candidates

James P. Szybist (Primary Contact), Derek A. Splitter

Oak Ridge National Laboratory
National Transportation Research Center Site
2360 Cherahala Blvd.
Knoxville, TN 37932
Phone: (865) 946-1514
Email: szybistjp@ornl.gov

DOE Technology Development Manager:
Kevin Stork

- Investigate the effect of EGR on PSHR in a boosted SI engine with realistic air handling boundary conditions
- Analyze the experimental results using chemical kinetic simulations with bio-fuel mechanisms from Lawrence Livermore National Laboratory ■

Introduction

The central fuel hypothesis of the Co-Optima program states that if we understand the critical fuel properties for engine performance, then fuels with those properties will provide comparable performance regardless of the chemical composition. However, it is not yet understood whether traditional fuel properties for SI engines are sufficient at characterizing anti-knock performance under boosted operating conditions. This is because both the RON and MON tests are conducted under naturally aspirated conditions, and as a result the pressure at a given cylinder temperature is higher. Boosted engines have a different trajectory in the pressure–temperature space, which causes them to interact with autoignition kinetics in a different regime than naturally aspirated engines have traditionally encountered. Further, boosted engines typically operate with highly retarded combustion phasing at high engine loads, which further alters the pressure–temperature trajectory relative to the RON and MON tests. FY 2016 efforts for this project were aimed at characterizing the autoignition propensity under boosted operating conditions for fuels with matched RON but varying S, and to use chemical kinetic simulations to understand the differences. Efforts continuing into FY 2017 are focused on the additional changes that EGR impart on the combustion system.

Approach

An experimental investigation was conducted with three fuels in a single-cylinder research engine with a modern direct injection fueling system operating at stoichiometric SI engine conditions. Three different fueling rates at 2,000 rpm with a fuel matrix designed to hold RON constant at 100 while varying the S were used. Complete fuel properties are shown in Table 1. The fueling rates were sufficient to produce nominal engine loads of 10 bar, 15 bar, and 20 bar indicated mean effective pressure, although the actual engine load depended on the combustion phasing, which was adjusted at each operating point to the knock-limited spark advance. At each condition, sweeps of intake air temperature were conducted. Cylinder pressure data was analyzed using standard combustion analysis techniques.

To provide more insight into the fuel-specific behavior, kinetic simulations were performed using CHEMKIN. All ignition delay simulations were performed under adiabatic conditions using the closed homogeneous reactor simulation with a constant volume under stoichiometric conditions with air. The gasoline surrogate mechanism from Lawrence Livermore National Laboratory, containing 1,389 species and 5,935 reactions [1], was used for the simulations. The kinetic formulations for each fuel is presented in Table 2.

Results

The knock limited spark advance is shown as a function of each fueling rate in Figure 1. Because each fuel was operated at knock-limited spark advance phasing, the fuel with the most advanced phasing was the most resistant to engine knock. The following observations can be made.

- At Condition A, iso-octane was the most knock resistant, followed by gasoline, with E40 as the most knock prone.
- At Conditions B and C, the fuel-specific trends were reversed where E40 was the most knock-resistant, and iso-octane was the most knock prone.

To understand why this is the case, pressure–temperature trajectory during compression for each engine condition is shown in Figure 2, stopping at the spark timing. Additionally, the pressure–temperature trajectory for the RON and MON tests up to top dead center is also shown. Condition A, which is the lightest load, has a pressure–temperature trajectory that is similar to the MON test. Thus, the fuel with the highest MON (iso-octane) has the best knock-resistance. In comparison, both Conditions B and C have pressure–temperature trajectories that have

Table 1. Properties of the Investigated Fuels

	Iso-Octane	Gasoline	E40
RON (ASTM D2699)	100	99.2	100
MON (ASTM D2700)	100	92.7	88
S (RON–MON)	0	6.5	12
Boiling point	99.3	N/A	N/A
IBP ^a	N/A	32.2	35.6
T10	N/A	56.1	54.9
T50	N/A	102.8	74.5
T90	N/A	109.4	145.2
FBPa	N/A	122.8	180.4
C wt %	84.2	85.5	70.8
H wt %	15.8	14.0	14.2
O wt %	0	0	15.0
LHV _a [MJ/kg]	44.3	43.586	36.76
LHV of stoichiometric mixture per kilogram of air [MJ]	2.94	2.98 ± 0.01 ^b	2.98
Aromatics	0	20	4
Saturates	100	80	52.3
Olefins	0	0	3
Ethanol	0	0	40.7

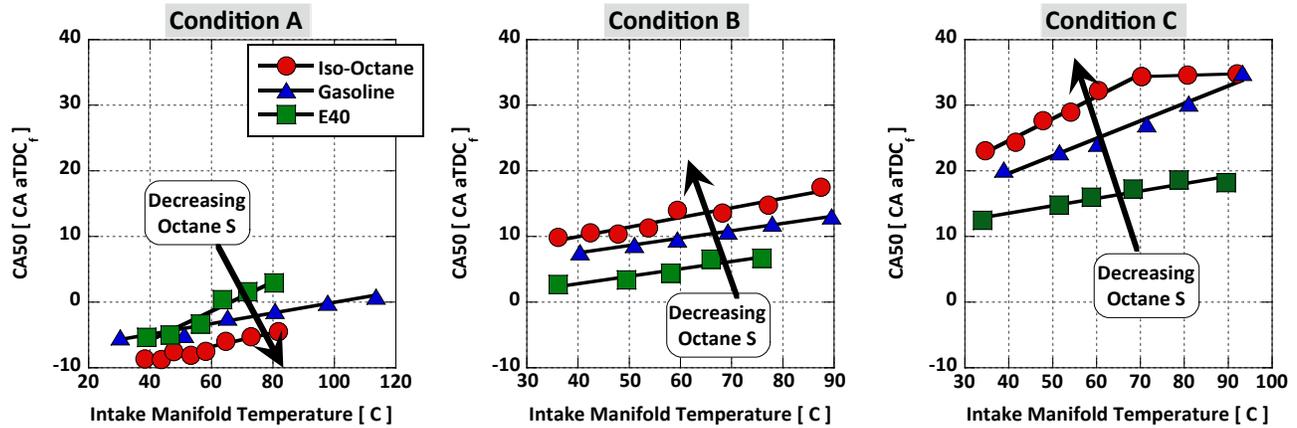
^aFBP = final boiling point; IBP = initial boiling point; LHV = lower heating value.

^bUncertainty is due to the elemental analysis (ASTM D 5291) accounting for only 99.5% of the fuel mass.

N/A – not available; E40 – 40% ethanol, 60% gasoline blend; T10 – temperature at 10% conversion; T50 – temperature at 50% conversion; T90 – temperature at 90% conversion

Table 2. Surrogate Formulations for the Chemical Kinetic Mechanisms

	Iso-Octane surrogate	Gasoline surrogate	E40 surrogate
Iso-octane (vol %)	100	62.6	36.0
N-heptane (vol %)	0	9.4	24
Toluene (vol %)	0	28	0
Ethanol (vol %)	0	0	40



CA - crank angle; aTDC - after top dead center

Figure 1. Crank angle at 50% burn (CA50) combustion phasing as a function of intake manifold temperature for each fuel for Condition A, Condition B, and Condition C

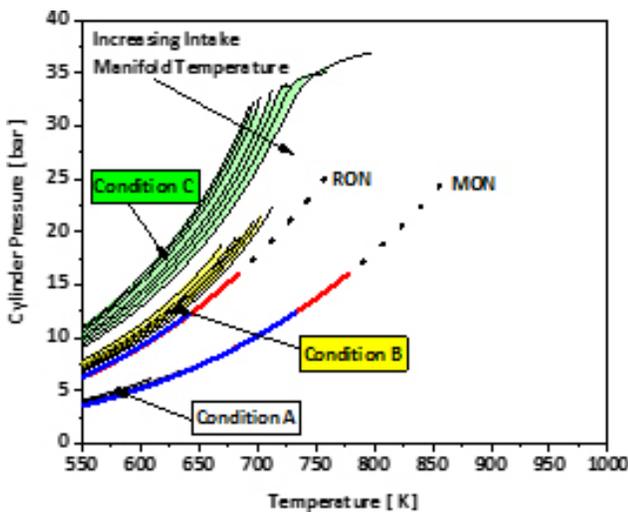


Figure 2. Iso-octane compressive temperature and pressure trajectories for the experimental conditions up to spark timing, as well as the RON and MON conditions. The experimental data include the compression process before spark ignition timing.

a higher pressure for a given temperature than either the RON or MON test. For these conditions, the fuel with the highest octane sensitivity has the highest resistance to knock and performs the best performance.

The lower resistance to knock can be attributed to the presence of PSHR. Figure 3 shows that as the intake manifold temperature is increased for iso-octane, PSHR develops. Initially the heat release rate (HRR) continually increases until the spark-induced flame propagation takes over. However, at sufficiently high temperatures there is a decrease in the HRR, indicative of the negative

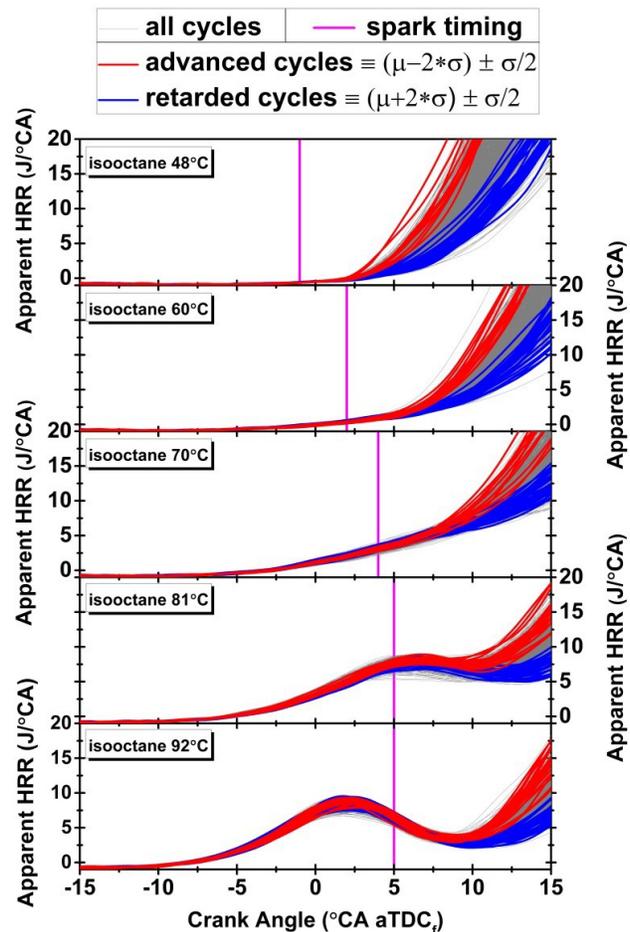
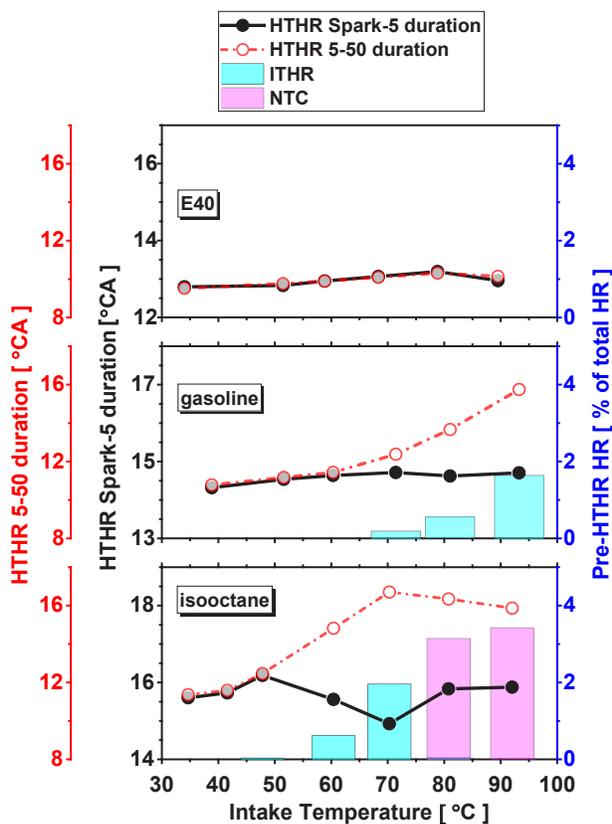


Figure 3. Individual cycle apparent HRR for iso-octane exhibiting heat release before spark discharge at Condition C intake manifold sweep. Advanced cycles (red), retarded cycles (blue), all cycles (grey), and spark timing (magenta).

temperature coefficient (NTC) regime. The amount of PSHR for each fuel, and whether there is NTC behavior, is shown in Figure 4. Iso-octane (lowest S) exhibits the highest amount of PSHR, whereas E40 (highest S) does not exhibit any PSHR.

Chemical kinetic simulations were used to identify regions of low temperature heat release (LTHR), which is the chemical phenomenon leading to PSHR, as shown in Figure 5 for iso-octane and gasoline. This region can be considered a region where heat release chemistry begins, but does not immediately result in complete combustion. Iso-octane, which has the lowest S, has the largest island of LTHR and the pressure–temperature trajectory for Condition C intersects this island of reactivity, leading to the PSHR observed in the experiments. E40 has a much smaller and lower magnitude island of LTHR. As a result, the experimental data does not exhibit any LTHR for this fuel.



HTHR – high temperature heat release; ITHR – intermediate temperature heat release

Figure 4. High-temperature combustion: 5%–50% mass fraction burned as a function of intake temperature (black), heat release before spark without NTC behavior (cyan bars), and heat release before spark with NTC behavior (magenta bars)

Complete documentation of these findings can be found in Szybist and Splitter [2]. These findings are providing new insights into how the kinetic autoignition processes relate to the pressure–temperature conditions that are relevant to modern boosted downsized engines. This is providing insight on how to operate modern engines and which regions of reactivity in the pressure–temperature space are most important for fuels to provide good performance. Continuing research focuses on studying fuel-specific behavior under boosted conditions with EGR present. The continuing work will include the Co-Optima core fuel matrix as well as several bio-fuel candidates proposed by

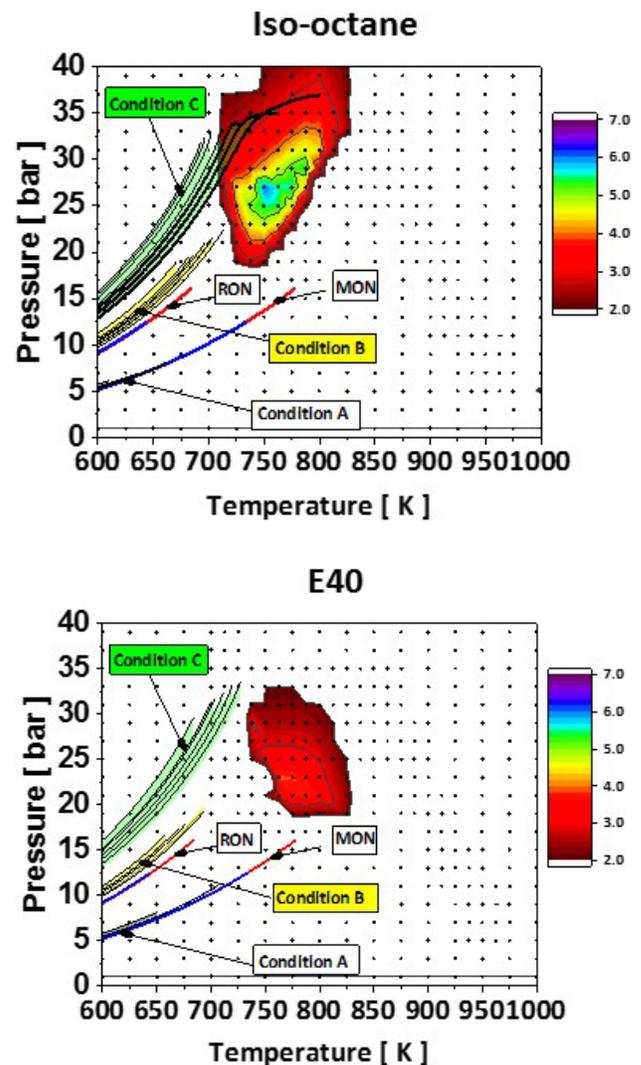


Figure 5. Ignition delay difference. Ignition delay defined by the final temperature inflection point minus the ignition delay defined as a 50 K temperature rise for iso-octane, gasoline, and E40 as a function of pressure and temperature. Experimental pressure and temperature trajectories are overlaid for Conditions A, B, and C.

the High Performance Fuels Co-Optima technical team. The work thus far indicates that the RON and MON fuel metrics may not sufficiently describe the knock propensity under boosted operating conditions, which is an important consideration for the Co-Optima effort. Additional insights will be provided on this in FY 2017.

Conclusions

- The ranking of knock propensity within a set of fuels with matched RON changes based on the operating conditions. Under conditions that are not boosted, the resistance to knock can be ranked using MON. However, under boosted operating conditions the ranking reverses and the fuels can be rated according to S.
- The PSHR was identified under boosted conditions for two of the fuels investigated. Chemical kinetic modeling was used to show that even though the RON of the fuels was the same, the chemical kinetic reactivity of the fuels at higher pressure conditions differed substantially, and that the PSHR could be attributed to the well-understood LTHR phenomenon.
- The results produced in FY 2016 indicate that RON and MON may not sufficiently describe a fuels knock propensity. This is an important consideration for the light-duty approach in Co-Optima since the path to higher efficiency is dependent on boosted operating conditions.

References

1. Mehl M., Pitz W.J., Westbrook C.K., Curran H.J. "Kinetic modeling of gasoline surrogate components and mixtures under engine conditions," *Proc. Comb. Inst.* 2011; 33(1), DOI:doi:10.1016/j.proci.2010.05.027.
2. Szybist, J., and Splitter, D., "Pressure and Temperature Effects on Fuels with Varying Octane Sensitivity at High Load in SI Engines," In Press. Accepted to *Combustion and Flame* in November 2016.
3. Szybist, J., and Splitter, D., "Pressure and Temperature Effects on Fuels with Varying Octane Sensitivity at High Load in SI Engines," In Press. Accepted to *Combustion and Flame* in November 2016.
4. Szybist, J., and Splitter, D., "Pressure and Temperature Effects on Fuels with Varying Octane Sensitivity at High Load in SI Engines," Presented at the Advanced Engine Combustion Bi-Annual Program Review Meeting, Southfield, MI, August 16, 2016.
5. Szybist, J., and Splitter, D., "Pressure and Temperature Effects on Fuels with Varying Octane Sensitivity at High Load in SI Engines," Presented at the ACEC Tech Team Meeting via Web Meeting, Southfield, MI, July 21, 2016.
6. Szybist, J., and Splitter, D., "Effects of Fuel Composition on EGR Dilution Tolerance in Spark Ignited Engines," Presented at the Advanced Engine Combustion Bi-Annual Program Review Meeting, Southfield, MI, February 9, 2016.
7. Sluder, S., Szybist, J., McCormick, R., Ratcliff, M., Zigler, B., "Exploring the Relationship Between Octane Sensitivity and Heat-of-Vaporization," Presented at the Advanced Engine Combustion Bi-Annual Program Review Meeting, Southfield, MI, February 9, 2016.
8. Szybist, J., Miles, P., Sjöberg, M., Zeng, W., McCormick, R., Zigler, B., Ratcliff, M., Wallner, T., and Ickes, A., "Understanding Octane Number and its Relevance to Modern and Emerging Engines," Presentation to the Co-Optima Stakeholders conference call and web meeting, November 17, 2015.
9. Szybist, J., Sluder, S., Ratcliff, M., Wallner, T., Splitter, D., Sjöberg, M., Ickes, A., Kolodziej, C., McCormick, R., Miles, P., "Co-Optimization of Fuels and Engines; Fuel Property and Advanced Engine Development Team Thrust I Engine Projects," 2016 DOE Vehicle Technologies Annual Merit Review, Project ID ACE015, presented June 9, 2016.

FY 2016 Publications/Presentations

1. Szybist, J. and Splitter, D., "Effects of Fuel Composition on EGR Dilution Tolerance in Spark Ignited Engines," *SAE Int. J. Engines*9(2):819–831, 2016, doi:10.4271/2016-01-0715.
2. Sluder, C., Szybist, J., McCormick, R., Ratcliff, M. et al., "Exploring the Relationship Between Octane Sensitivity and Heat-of-Vaporization," *SAE Int. J. Fuels Lubr.* 9(1):80–90, 2016, doi:10.4271/2016-01-0836.

Special Recognitions and Awards/ Patents Issued

1. USCAR Recognition Award for contributions to the U.S. DRIVE ACEC Fuels Roadmap Sub-Team.
2. SAE Forest R. McFarland Award for outstanding contributions in planning, development, and dissemination of technical information.

II.7 Extension of the Particulate Matter Index (PMI) for Gasoline Blended with Oxygenates

Overall Objectives

- Characterize qualitatively and quantitatively how oxygenated blending components affect the efficacy of the particulate matter index (PMI), a model which has demonstrated high accuracy in predicting particulate matter (PM) emissions from petroleum-based gasoline
- Develop improvements to the PMI model that account for fuel property and fuel chemistry effects on PM emission that are unique to oxygenate–gasoline blends

Fiscal Year (FY) 2016 Objectives

The National Renewable Energy Laboratory will quantify the interactions between ethanol level and aromatic hydrocarbons covering a range of vapor pressures on PM emissions from a gasoline direct injection (GDI) engine.

FY 2016 Accomplishments

- A full factorial experimental design of fuel composition was conceived to test the null hypothesis that gasolines having high heat of vaporization (HOV), in this case from adding ethanol, and low vapor pressure aromatics do not increase PM emissions.
- The fuels were blended and analyzed by a gas chromatography method providing detailed hydrocarbon analysis (DHA); from this the PMIs and HOVs of the fuels were computed.
- The advanced distillation curve (ADC) method was then used to characterize the changes in evaporated fuel composition as a function of percent fuel distilled. A new finding from the ADC characterization was that ethanol blending delayed the evaporation of aromatics in the fuel to the end of the distillation process.
- Five of the fuels comprising a partial factorial design (one face of the full factorial design) were then combusted in a single-cylinder, GDI engine, and the PM emissions were measured at six distinct operating conditions.
- Preliminary data analysis indicates that gasoline having both high HOV and low vapor pressure aromatics fueling a GDI engine at 2,500 revolutions per minute (rpm) produces higher PM emissions than predicted by the fuel's PMI. Thus, it appears that the null hypothesis must be rejected for some cases investigated, and

**Matthew A. Ratcliff (Primary Contact),
Jonathan Burton, Petr Sindler and
Robert L. McCormick**

National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-4438
Email: matthew.ratcliff@nrel.gov

DOE Technology Development Manager:
Kevin Stork

therefore development of an improved PMI model seems warranted.

Future Directions

- Perform comprehensive data analysis from PM emissions measurements and obtain additional emissions data from other concentrations of the aromatic hydrocarbons per the full factorial design
- Obtain PM emission data from one or two blends using an iso-paraffin with the same vapor pressure as one aromatic in the experimental design; these blends will serve as control fuels for comparison with aromatic blend results
- Investigate oxygenate chemistry effects on PM emissions using oxygenates having the same vapor pressures and double bond equivalents (DBEs) as the single-ring alkyl aromatics in the present study
- Investigate alternate formulations of PMI to more accurately predict a blend component's propensity to form soot ■

Introduction

There are conflicting results in the literature on the impacts of ethanol blended-gasoline on PM emissions. Many or most studies show a reduction in PM as the ethanol (which has near zero soot forming potential) level increases [1–3]. This is usually attributed in “splash-blended” fuel studies to ethanol's dilution of gasoline hydrocarbons that have a high potential to form soot. However, other studies show increased PM

under some operating conditions. For example, He and coworkers observed increased PM for an E20 blend at high load, and suggested that ethanol's high HOV slowed fuel evaporation from piston and cylinder surfaces [4]. Similar observations have been made in other studies where blending ethanol into gasoline results in higher PM emissions [5,6]. Thus, one objective of this project is to better understand these seemingly contradictory findings by clarifying the interactions between a fuel's HOV, the presence of low vapor pressure aromatic hydrocarbons, and engine operating conditions.

The PMI [7,8] is calculated from the DHA results for each fuel blend according to:

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

DBE represents the tendency for individual fuel components to form soot and is the sum of rings and unsaturations in the fuel molecule: $DBE = (2C + 2 - H)/2$. Vapor pressure at 443 Kelvin ($VP(443K)$) represents the tendency for individual fuel components to evaporate. Fuel components with low $VP(443K)$ increase PMI because their vaporization is relatively slow, and they may therefore not fully evaporate and mix with air during engine cycle time scales. Locally heterogeneous combustion produces PM.

The PMI model has a widely demonstrated utility for accurately predicting and ranking the PM potential of petroleum-based gasolines. However, a recent study by our group demonstrated that PMI can underpredict PM emissions from some non-ethanol oxygenate fuel chemistries [9]. A review of the literature indicates a variety of chemical routes to PM precursors from oxygenates that do not exist, or are improbable for hydrocarbons. Consequently, traditional assignment of DBE values (the compound-specific soot forming tendency factors in the PMI model) to oxygenate components can be inaccurate. So, a second objective of this project is to identify a metric that more accurately captures the soot forming potential of a wide range of fuel chemistries beyond hydrocarbons. Possibilities include yield sooting index [10], smoke point, and oxygen extended sooting index [11].

All contemporary commercial gasolines have HOVs in the 350–400 kJ/kg range. Therefore the impact of HOV on the $VP(443K)$ term in the PMI model is essentially constant because the temperature of the fuel molecules after evaporation is invariant (all else being equal). If, however, the HOV of a conventional gasoline was

increased (e.g., by blending larger volumes of ethanol), and was then used in a GDI engine where evaporative cooling by the fuel is intentionally maximized, the combined effect may be higher PM emissions, i.e., the fuel–air charge temperature reduction provided by high HOV, coupled with a fuel injection strategy optimized to capture this cooling in-cylinder can significantly reduce the vapor pressure of the high boiling aromatic compounds (or hypothetically, high boiling oxygenates). Inhibition of fuel vaporization may produce heterogeneous air–fuel mixtures which are the major source of PM.

Thus, PMI as presently defined may be inadequate to predict the PM potential from the range of oxygenates and HOVs being investigated in the Co-Optima program, and the ultimate objective of this project is to refine the PMI model to accurately predict fuel PM emission potential over a wider range of fuel chemistry and HOV than conventional gasoline.

Approach

PM emissions were measured from GDI engine experiments using fuels from a partial factorial design (Figure 1), intended to test the hypothesis that increasing fuel HOV (via increasing ethanol content) while maintaining constant aromatic content can cause PM emissions to increase. Stated another way, the designed experiment tested the null hypothesis that a fuel's HOV and the vapor pressure of late boiling, single-ring aromatic hydrocarbons do not interact to affect PM emissions. The partial factorial fuel matrix derives from a full factorial design that adds the dimension of aromatic concentration (planned future work). The chosen gasoline blendstock for these experiments was the low aromatic, high octane Fuel for Advanced Combustion Engines (FACE) Gasoline B, into which selected boiling point aromatics and ethanol were blended.

Before the PM measurements commenced, PMI and HOV were computed based on the fuel's DHA (per ASTM method D6729), as described in our previous publications [9,12]. In addition, 15 fuel blends comprising the full factorial design were characterized by the ADC method [13] in which the composition of each distillate fraction was quantified by DHA using gas chromatography. Although details of the ADC results are not reported here, ADC quantified ethanol's impacts on fuel evaporation temperatures and the composition of the evaporating fluid across the distillation temperature range [14]. A new finding from the ADC characterization was that ethanol blending delayed the evaporation of aromatics in the fuel to the end of the distillation process. This has

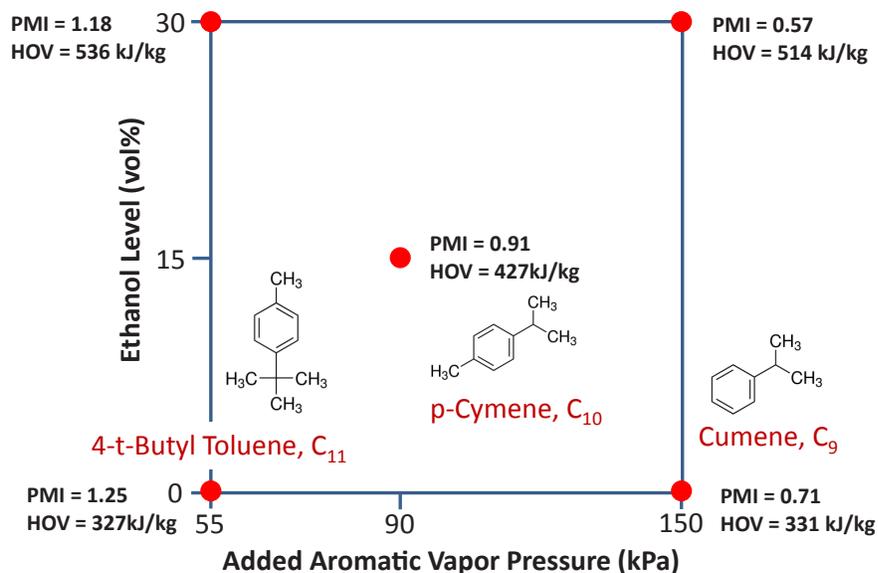


Figure 1. Partial factorial experimental design for fuel blends. Tested blends are indicated by red dots, with associated PMI and HOV values from detailed hydrocarbon analyses. Aromatic hydrocarbon vapor pressures on the X-axis are at 443 K.

been tentatively interpreted as a preference by ethanol to form azeotropes with the paraffins that are predominant in FACE B. Thus, there appears to be a previously unappreciated physicochemical factor arising from ethanol blending, in addition to charge cooling by virtue of its high HOV, which may potentially increase PM emissions.

PM mass emissions were measured with an AVL Micro-Soot Sensor (MSS) connected to the raw engine exhaust providing real-time PM-mass. The MSS contains its own built-in dilution system, which was nominally set to an 8:1 ratio. Particle number and particle size distributions were also measured (but not reported here) by a TSI Fast Mobility Particle Sizer (FMPS) model 3091. The FMPS measures particle number distribution for particle diameters between 5.6 nm to 560 nm with a 32-channel resolution. The exhaust sample for the FMPS was provided by a Dekati FPS-4000 two-stage exhaust sample dilution system in series with a Dekati Thermodenuder, as described in our earlier work [9].

Results

PM emissions were measured using National Renewable Energy Laboratory's single-cylinder, GDI engine. Intake air temperature was fixed at 35°C. Six engine operating conditions were investigated (see Table 1), including two baseline conditions (A = 2,500 rpm, 13 bar net mean effective pressure [NMEP], and D = 1,500 rpm, 10 bar NMEP) using single injection events early in the

intake stroke (start of injection [SOI] = 280° before top dead center [BTDC]). This SOI, however, minimized or avoided spray impingement on the piston [4].

Steady-state PM measurements from the designed fuels are shown in Figure 2. Emission results from baseline conditions A and D are the most direct test of the HOV versus PM hypothesis. The results of multiple regression analysis for the factorial designed fuel matrix used for conditions A and D are shown in Table 2. For condition A, the model has a modest goodness of fit (r^2) suggesting that a larger fuel matrix (additional ethanol levels, for example) could improve the model. Coefficients for both ethanol content (a surrogate for HOV) and aromatic vapor pressure are significant with very low p-values, which support rejection of the null hypothesis, at least for this engine operating condition.

At condition D, goodness of fit is poor and the coefficient for ethanol content is not significant. While the coefficient for aromatic vapor pressure is significant, its value is less than that for condition A. Compared to condition A, the amount of fuel injected for D was less (shorter injection pulse widths for the lower load) and the time available for evaporation between injection and ignition was 62% longer (29 ms vs. 18 ms) because of the slower engine speed. Consequently, there was more time for heat transfer, fuel evaporation, and mixing, perhaps limiting the effects of HOV and aromatic vapor pressure. Condition E used the same speed and load as condition D,

Table 1. Engine Operating Conditions for PM Measurements

Test Condition	Speed – Load (rpm –bar NMEP)	Target λ (or CO %)	SOI (°BTDC)	Spark Timing (°BTDC)	CA50 (°ATDC)	Objective
A	2500 - 13	1.0 - 1.01	280	6.5	22 ± 2	Base condition, high load with late combustion phasing. Links to previous data set
B	2500 - 13	1.0 - 1.01	Split Injection 50:50 @ 280 and 220	≈9	22 ± 2	Effect on PM by minimizing fuel impingement. Compare with A
C	2500 - 13	1.0 - 1.01	Split Injection 80:20 @ 280 and 80. Fix 2 nd injection pulse width = 0.68 ms	<8	22 ± 2	Effect on PM from stratified charge combustion. Compare with A
D	1500 - 10	1.0 - 1.01	280	15	7.5 ± 1.5	Base condition at MBT combustion phasing. Compare with A, E and F
E	1500 - 10	0.92 (3.0% CO)	280	≤15	7.5 ± 1.5	Fuel-rich combustion emulating acceleration. Compare with D
F	1500 - 10	1.0 - 1.01	Split Injection 80:20 @ 280 and 80. Fix 2 nd injection pulse width = 0.57 ms	15	7.5 ± 1.5	Effect on PM from stratified charge combustion. Compare with D and C

ATDC – after top dead center; CA50 – crank angle for 50% mass of fuel burned; CO – carbon monoxide; λ – actual air-to-fuel ratio / stoichiometric air-to-fuel ratio; MBT – maximum brake torque

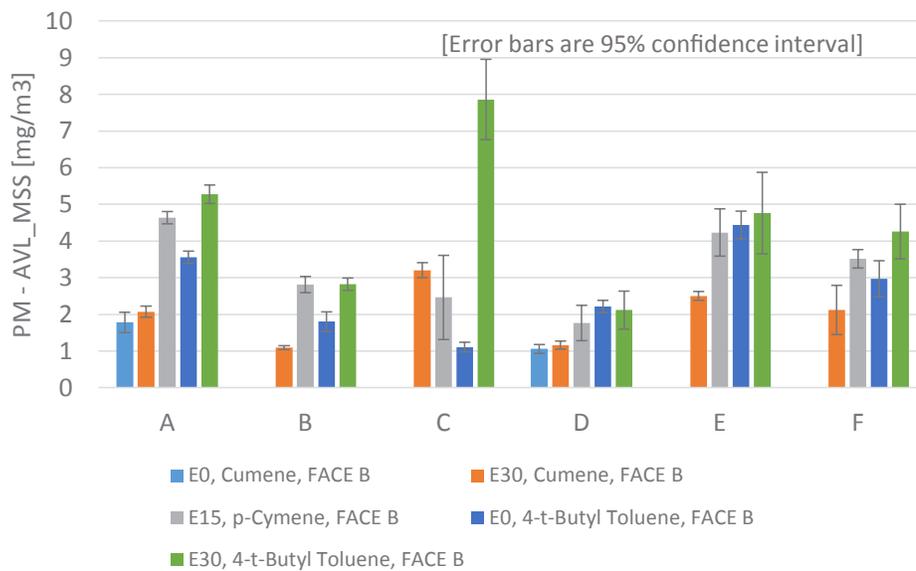


Figure 2. PM emissions measured by an AVL MSS at six engine operating conditions (A-F)

but was fuel-rich ($\lambda = 0.92$). Overall the PM emissions were higher as expected.

Table 2. Results of Multiple Regression Analysis of the Data for Conditions A and D

	Condition A: 2,500 rpm/13 bar NMEP	Condition D: 1,500 rpm/10 bar NMEP
Adjusted r^2	0.79	0.42
Ethanol vol% coefficient	0.0355	0.0013
Ethanol vol% p-value	<0.01	0.78
Aromatic vapor pressure coefficient	-0.0262	-0.0094
Aromatic vapor pressure p-value	<0.01	<0.01

Figure 3 shows the relationship between PMI and PM emissions for all fuels at conditions A and D. A reasonably strong linear correlation is shown for condition D, consistent with the idea that fuel HOV is having little effect on PM at the lower engine speed and load. For condition A, the correlation is very poor, indicating that PMI does not adequately describe tendency to form PM for these fuels at this operating condition.

Looking in more detail at the results for condition A (Figure 2), the comparison of E0 to E30 (30% ethanol, 70% gasoline blend) for the t-butyl-toluene fuels shows a clear increase in PM from the high HOV blend, while there is no significant difference for E0 versus E30 from the cumene blends. The vapor pressure of cumene may be sufficiently high that increased HOV cannot inhibit its evaporation and thereby produce more PM, under these engine operating conditions. These results suggest a threshold vapor pressure for aromatics where a PM increase becomes significant for some level of HOV. The increase in PM emissions from the E30 + t-butyl-toluene blend at condition A may thus be the result of three factors: (1) ethanol's suppression of aromatic evaporation while both are present in the fuel, (2) a reduction in available heat and temperature for aromatic evaporation after the ethanol evaporates, and (3) insufficient time at 2,500 rpm to allow heat transfer for aromatic evaporation.

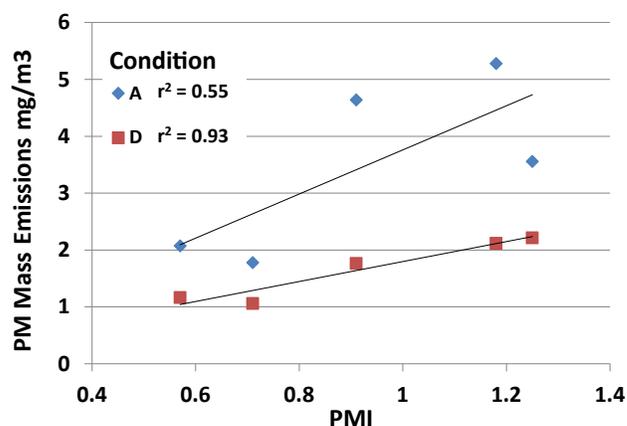


Figure 3. Plot of measured PM vs. PMI for operating conditions where start of injection was 280° BTDC

Conditions B and C (at 2,500 rpm and 13 bar) used split fuel injection strategies. For condition B, the injection was split 50:50, early (SOI = 280° BTDC) and late (SOI = 220° BTDC) in the intake stroke with the intention to reduce spray penetration length and increase charge cooling. As Figure 2 shows, the consistent result of this injection strategy was a reduction of PM emissions in all cases, relative to the single injection used in condition A. Presumably this PM reduction came from shorter injection durations and the consequent shorter spray penetration lengths, leading to less spray contact with the cylinder surfaces and more homogeneous fuel-air mixtures. For condition C, the fuel injection was split 80:20, with the majority of the fuel injected during air intake at SOI = 280° BTDC. The 20% fraction was injected late in the compression stroke (80° BTDC) to emulate a stratified charge injection strategy (albeit at globally stoichiometric combustion), with high potential for fuel spray impingement on the piston. Condition F used the same injection strategy but at the lower speed and load. Fuel effects from these experiments are complex and will require additional analysis.

Conclusions

While in-depth analysis of the emission results is ongoing, we can offer these preliminary conclusions:

- At 2,500 rpm the null hypothesis that a fuel's HOV and the vapor pressure of late boiling, single-ring aromatic hydrocarbons do not interact to affect PM emissions must be rejected.
- In contrast, at the slower engine speed of 1,500 rpm there is significantly more time for heat transfer, evaporation, and air mixing, and here the null hypothesis is confirmed.

- There appears to be a threshold vapor pressure for aromatics, where a PM increase can become significant for some level of HOV, and given some time constraint for heat transfer and evaporation.

References

1. Maricq, M.M.; Szente, J.J.; Jahr, K. 2012. "The impact of ethanol fuel blends on PM emissions from a light-duty GDI vehicle." *Aerosol Sci. Technol.* **46** (5): 576–583.
2. He, X., Ireland, J.C., Zigler, B.T., Ratcliff, M.S., Knoll, K.E., Alleman, T.L., Tester, J.T. 2010. "The Impacts of Mid-level Biofuel Content in Gasoline on SIDI Engine-out and Tailpipe Particulate Matter Emissions." SAE Techn. Pap. doi: 10.4271/2010-01-2125.
3. Fatouraie, M., Wooldridge, M.S., Petersen, B.R., Wooldridge, S.T. 2015. "Effects of Ethanol on In-Cylinder and Exhaust Gas Particulate Emissions of a Gasoline Direct Injection Spark Ignition Engine," *Energy Fuels* **29**: 3399–3412.
4. He, X., Ratcliff, M.A., and Zigler, B.T. 2012. "Effects of Gasoline Direct Injection Engine Operating Parameters on Particle Number Emissions," *Energy Fuels* **26**:2014–2027.
5. Butler, A.D., Sobotowski, R.A., Hoffman, G.J., and Machiele, P. 2015. "Influence of Fuel PM Index and Ethanol Content on Particulate Emissions from Light-Duty Gasoline Vehicles," SAE Technical Paper 2015-01-1072.
6. Storch, M., Koegl, M., Altenhoff, M., Will, S., and Zigan, L. 2016. "Investigation of soot formation of spark-ignited ethanol-blended gasoline sprays with single- and multi-component base fuels," *Applied Energy* **181**:278–287.
7. Aikawa, K., Sakurai, T., and Jetter, J.J. 2010. "Development of a Predictive Model for Gasoline Vehicle Particulate Matter Emissions," *SAE Int. J. Fuels Lubr.* **3**(2):610–622. doi:10.4271/2010-01-2115.
8. Aikawa, K., and Jetter, J.J. 2013. "Impact of Gasoline Composition on Particulate Matter Emissions from a Direct-Injection Engine: Applicability of Particulate Matter Index," *Int. J. Eng. Res.* **15**(3):298–306. doi: 10.1177/1468087413481216.
9. Ratcliff, M.A., Burton, J., Sindler, P., Christensen, E., Chupka, G.M., Fouts, L., McCormick, R.L. 2016. "Knock Resistance and Fine Particle Emissions for Several Biomass-Derived Oxygenates in a Direct-Injection Spark-Ignition Engine" *SAE Int. J. Fuels Lubr.* **9**(1):59–70. doi:10.4271/2016-01-0705.
10. McEnally, C.S., Pfefferle, L.D. 2007. "Improved Sooting Tendency Measurements for Aromatic Hydrocarbons and their Implications for Naphthalene Formation Pathways," *Combust. Flame* **148**, 210–222.
11. Barrientos, E.J., Anderson, J.E., Maricq, M.M., and Boehman, A. 2016. "Particulate Matter Indices Using Fuel Smoke Point for Vehicle Emissions with Gasoline, Ethanol Blends, and Butanol Blends," *Combust. Flame*, **167**, 308–319.
12. Chupka, G.M., Christensen, E., Fouts, L., Alleman, T.L., Ratcliff, M., McCormick, R.L. 2015. "Heat of Vaporization Measurements for Ethanol Blends Up To 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines" *SAE Int. J. Fuels Lubr.* doi:10.4271/2015-01-0763.
13. Smith, B.L., Bruno, T.J. 2007. "Improvements in the measurement of distillation curves. 3. Application to gasoline and gasoline + methanol mixtures," *Ind. Eng. Chem. Res.* **46**, 297–309.
14. Burke, S.C., Ratcliff, M.A., McCormick, R.L., Rhoads, R., and Windom, B. "Distillation-based droplet modeling of non-ideal oxygenated gasoline blends: investigating the role of droplet evaporation on PM emissions," SAE Technical Paper 17PFL-1152, to be published for SAE World Congress, April 2017.

FY 2016 Publications/Presentations

1. Burke, S.C., Ratcliff, M.A., McCormick, R.L., Rhoads, R., and Windom, B., "Distillation-based droplet modeling of non-ideal oxygenated gasoline blends: investigating the role of droplet evaporation on PM emissions," SAE Technical Paper 17PFL-1152, to be published for SAE World Congress, April 2017.

II.8 GDI Fuel Effects on PM Emissions

Overall Objectives

- The overall objective of the Co-Optimization of Fuels & Engines Initiative (Co-Optima) is to cooperatively develop emerging biofuels and advanced engines to bring these technologies to the market sooner to realize a reduction in petroleum consumption.
- This project aims to investigate the validity of the Co-Optima central fuel hypothesis, which states that a fuel candidate should perform in a manner commensurate with its properties regardless of its chemistry.
- This project is investigating the impacts of candidate biofuel blends on the generation and composition of particulate matter (PM) emissions from gasoline direct injection (GDI) engines and assessing the potential for mitigation of GDI PM with emissions controls.

Fiscal Year (FY) 2016 Objective

Oak Ridge National Laboratory will quantify the impacts of gasoline–alcohol blends on the oxidation behavior of PM from a GDI engine.

FY 2016 Accomplishments

- Evaluated soot oxidation kinetics for PM collected from a GDI engine operating on both 100% gasoline (E0) and a 30% ethanol–gasoline blend (E30)
- Demonstrated that GDI PM becomes more difficult to oxidize as regeneration progresses, unlike diesel PM which has a near constant activation energy
- Determined the soot layer thickness inside the gasoline particulate filter (GPF) using neutron imaging

Future Directions

- Continue neutron imaging studies of soot layer thickness
- Characterize PM emissions from a GDI engine operating on three candidate gasoline biofuel blends ■

Introduction

The central fuel hypothesis of the Co-Optima program states that if we understand the critical fuel properties for engine performance, then fuels with those properties will provide comparable performance regardless of the chemical composition. However, the same cannot be

**John M.E. Storey (Primary Contact),
Melanie Moses-DeBusk,
Samuel A. Lewis,
Raynella M. Connatser, Josh A. Pihl,
Todd J. Toops, and Charles E.A. Finney**

Oak Ridge National Laboratory
National Transportation Research Center
PO Box 2008, MS 6472
Oak Ridge, TN 37831-6472
Phone: (865) 946-1232
Email: storeyjm@ornl.gov

DOE Technology Development Manager:
Kevin Stork

said for emissions performance, particularly for PM emissions. The Particulate Matter Index [1] uses physical and chemical properties of the fuel to predict *relative* PM emissions from spark-ignited engines, and has been shown to be quite robust for port fuel injected vehicles [2]. However, fuels containing oxygen and vehicles with GDI engines may not follow the trends predicted by the Particulate Matter Index. PM emissions from GDI engines can be affected by the oxygen in the fuel, the aromatic nature of the biofuel and the blend stock, and the specifics of the combustion and emissions control strategies [3–4]. This activity is assessing the impacts of candidate biofuel blends on the generation and composition PM emissions from GDI engines, and the potential mitigation of GDI PM with emissions controls. While the focus in FY 2016 was on ethanol as a blending component, other blending components will be incorporated into the studies in future years. Beyond physical and chemical characterization of the engine PM, this sub-task is also examining whether the performance of exhaust particulate filters may be enhanced through the use of biofuel–gasoline blend fuels. The different properties of the soot from biofuel blends may enhance soot oxidation kinetics and/or lower oxidation light-off temperatures, which can lead to higher efficiency of the emissions control strategy.

Approach

The experimental approach was designed to examine the effects of gasoline–alcohol blends on PM characteristics. GDI engines generate the most exhaust PM under fuel-rich conditions, typical of start-up and acceleration. Thus,

for this study, the air-to-fuel ratio, as well as the real-time soot concentration, was measured during acceleration transients to determine a representative steady-state operating point. The engine was a 2.0-L light-duty engine modified with an engine control system to allow changes in injection and ignition timing [5]. Gasoline, as well as gasoline blended with ethanol, were used as fuels. Fuels included unleaded gasoline (E0, 87 Anti-Knock Index), 30% ethanol and 70% E0 by volume (E30). For the soot oxidation studies described below, PM was collected in miniature GPF substrates.

Soot oxidation experiments were carried out for GDI PM collected on uncoated GPF cores mounted directly in the exhaust as shown in Figure 1a. The soot oxidation kinetics experiments [6] use pulsed oxidation at different temperatures to characterize the activation energy (reactivity) of the soot generated from the two fuel blends. Additional GPF cores, generated during the same exposure experiments, underwent measurement with neutron imaging at the High Flux Isotope Reactor (HFIR) to determine the soot layer thickness (Figure 1b). The radioactivity of the imaged core is negligible after a few weeks allowing a further oxidation step and subsequent imaging of the same core to identify oxidation effects on the soot layer.

Results

Previous reports have detailed the physical and chemical characteristics of the GDI PM generated in these experiments [5]. This report focuses on the characterization of the soot layer collected in the GPF. Because spark ignition engines tend to run at higher temperatures than diesel engines, the soot may not always build up in a layer, but may instead be constantly regenerating [7]. Nevertheless, by carefully measuring the

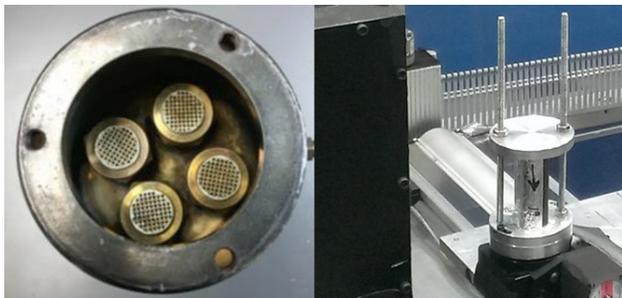


Figure 1. (a) Exposure apparatus for the GPF cores. This fixture was mounted in a slipstream of the exhaust from the GDI engine. (b) A single GPF core is shown mounted for neutron imaging at the Oak Ridge National Laboratory HFIR.

soot layer in the GPF, a better understanding of the soot oxidation behavior can be obtained.

Neutrons are absorbed more strongly by light elements like hydrogen and carbon than by the heavier elements in the GPF substrate material. This enables the layer to be imaged and the thickness determined along the length of the core. After removal and subsequent oxidation, the cores are returned to the HFIR and imaged again. Figure 2 shows the results for three neutron imaging sessions on the same set of cores collected during GDI operation with both E0 and E30. The first oxidation results in the removal of 20% of the soot (20% regen curve), and the second oxidation results in 40% removal (40% regen curve). The thickness increases along the length of the core as expected, since the plug is at the end of the core and the relationship between thickness and length is fairly constant between oxidation steps. However, there is a noticeable difference between the cores generated by the two fuels. After the first oxidation step, the E0 20% regen curve indicates a noticeable drop in the soot thickness

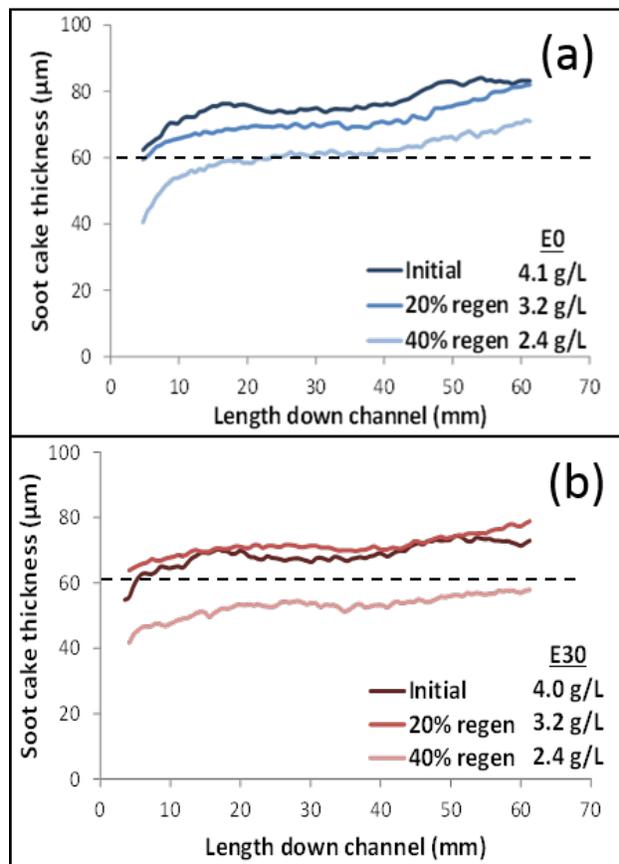


Figure 2. (a) Soot layer thickness as a function of axial length for a GPF core exposed to GDI engine exhaust with E0 fuel. (b) Soot layer thickness as a function of axial length for a GPF core exposed to GDI engine exhaust with E30 fuel.

which is followed by a continued reduction between the 20% and 40% regen curves which also show a relatively consistent spacing throughout the length of the GPF core (Figure 2a). In contrast, the E30 curve shows that there was very little loss of thickness despite the removal of 20% of the carbon (Figure 2b). The subsequent loss of thickness from 20% to 40% regen was greater than that observed for E0 but still consistent along the length of the core. These data thus imply that there is a larger amount of absorbed hydrocarbon (HC) in the E30 soot layer than in the E0 soot layer. Absorbed HC should be easier to oxidize than the more refractory soot structure, thus the implication of Figure 2b is that the first 20% of carbon removal results in the oxidation of the absorbed HCs which desorbed without impacting the soot thickness. The greater reduction in thickness observed after 40% regen for both the E0 and E30 sample is potentially the result of the soot layer collapsing. After further oxidation, additional neutron imaging of these two cores will show how the soot layer removal continues.

Oxidation experiments were performed on separate cores collected at the same time as the cores in Figure 2, but the kinetic oxidation behavior was studied at each of the similar regen steps up to about 80% regeneration (Figure 3). In addition, data from a study by Pihl et al. [6] on diesel soot oxidation is also included in Figure 3 (curve CDC). The key finding is that both the E0 and E30 GDI PM become more refractory (have a higher E_A) as the soot is oxidized, unlike the diesel PM which has the same

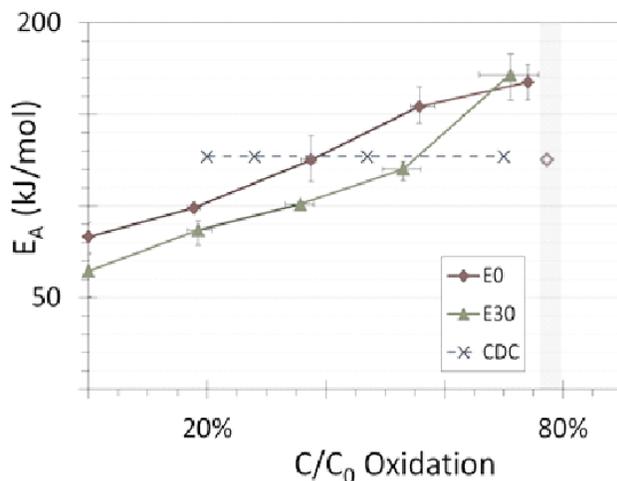


Figure 3. Activation energy (E_A) as a function of soot burned for soot generated in a GDI engine with E0 and E30 and collected in a GPF core. The conventional diesel combustion (CDC) curve is replotted from Pihl et al. [6] and shows E_A as a function of soot burned for soot generated in a diesel engine and collected in a GPF core.

reactivity (constant E_A) as the soot is removed. Initially, both the E0 and E30 PM have lower E_A than diesel PM, but, by the 80% oxidation step, the E_A has increased well above the value for diesel soot. This indicates that the GDI soot layer has become more refractory as a result of the oxidation. Figure 3 also illustrates the overall lower reactivity of E30 soot than E0 and diesel soot. For the first two oxidation steps, the lower E_A is consistent with Figure 2. Absorbed HC would have higher reactivity than the solid soot. The overall lower reactivity for E30 shown in Figure 3 may indicate a difference in the soot structure as well. Storey et al. [5] showed that oxygen was incorporated into the backbone of the E30 soot structure whereas it was absent from the E0 soot. The oxygen in the soot structure would likely lower its E_A .

Conclusions

- Neutron imaging at Oak Ridge National Laboratory allows a unique look inside the GPF cores to identify regeneration effects on soot layer thickness.
- GDI soot becomes more refractory as it is oxidized.
- E30 fuel tends to lower the reactivity of the soot layer in comparison to E0.

References

1. Aikawa, K., Sakurai, T., and Jetter, J., *SAE Int. J. Fuels Lubr.* 3(2):610–622, 2010, doi:10.4271/2010-01-2115.
2. Khalek, I., Bougher, T., and Jetter, J., *SAE Int. J. Fuels Lubr.* 3(2):623–637, 2010, doi:10.4271/2010-01-2117.
3. Storey, J., Barone, T., Norman, K., and Lewis, S., *SAE Int. J. Fuels Lubr.* 3(2):650–659, 2010, doi:10.4271/2010-01-2129.
4. Ratcliff, M., Burton, J., Sindler, P., Christensen, E. et al, *SAE Int. J. Fuels Lubr.* 9(1):59–70, 2016, doi:10.4271/2016-01-0705.
5. Storey, J.M.; Lewis, S. A.; Szybist, J.; Thomas, J.; Barone, T. Eibl, M.; Nafziger, E.; Kaul, B. *SAE Int. J. Fuels Lubr.* 7 (2): 2014. doi:10.4271/2014-01-1606.
6. Pihl, J.A; Lewis, J.A.; Toops, T.J.; Adelman, B.J.; Derybowski, E.M. (2013) *Top. Catal.* 56:499. DOI 10.1007/s11244-013-0005-6.
7. Lambert, C.K.; Bumbaroska, M.; Dobson, D.; Hangas, J.; Pakko, J.; Tennison, P. *SAE Int. J. Engines* 9(2): 2016, doi:10.4271/2016-01-094.

FY 2016 Publications/Presentations

1. Moses-DeBusk, M., Storey, J.M., Pihl, J.A. "Reactivity of GDI Soot on Particulate Filters: the changing landscape of vehicle PM." Oral presentation at 2016 CLEERS Workshop, April 6–8, 2016, Ann Arbor, MI.
2. Lucachick, G., Curran, S., Storey, J., Prikhodko, V., Northrop, W.F. "Volatility characterization of nanoparticles from single and dual-fuel low temperature combustion in compression ignition engines," *Aerosol Sci. Tech.* **50** (5): 436–447. 2016.
3. Storey, S.J., Curran, S., Lewis, S., Barone, T.L., Dempsey, A.B., Moses-DeBusk, M., Hanson, R.M., Prikhodko, V.Y., Northrop, W.F., "Evolution and current understanding of physicochemical characterization of particulate matter from reactivity controlled compression ignition combustion on a multi-cylinder light-duty engine," *International Journal of Engine Research*, 2016. doi:10.1177/1468087416661637.

II.9 Fuel Compatibility and Opportunities with Emissions Controls

Overall Objectives

- The overall objective of the Co-Optimization of Fuels & Engines Initiative (Co-Optima) is to cooperatively develop emerging biofuels and advanced engines to bring these technologies to the market sooner to realize a reduction in petroleum consumption.
- This project aims to investigate the compatibility of Co-Optima fuel candidates with emissions control systems and to identify opportunities for alternative emissions control strategies based on novel fuel chemistry.
- This project is investigating the following questions:
 - Is the catalytic reactivity of Co-Optima candidate fuel components sufficient to allow continued use of current emissions control technologies for both stoichiometric and lean operation?
 - Do the Co-Optima candidate fuel components create opportunities for alternative low-cost lean exhaust emissions control strategies, such as alcohol selective catalytic reduction (SCR) of NO over a silver-based catalyst?
 - Does the process for creating and refining the candidate Co-Optima fuel components introduce trace level impurities into fuel blends that could poison emissions control catalysts?

Fiscal Year (FY) 2016 Objectives

- Formulate strategy to measure catalytic light-off temperature reactivity for new Co-Optima fuel components and evaluate the impact on total hydrocarbon (THC) emissions during cold start operation
- Investigate potential benefits of a dual SCR configuration using both Ag- and Cu- containing catalysts for SCR control of lean NO_x emissions by alcohol-containing fuels
- Report compatibility findings from legacy project on trace elements associated with biodiesel production

FY 2016 Accomplishments

- Completed study on an automated synthetic exhaust flow reactor evaluating the benefits of a dual SCR

Todd J. Toops (Primary Contact), Josh A. Pihl, D. William Brookshear

Oak Ridge National Laboratory
2360 Cherahala Boulevard
Knoxville, TN 37932

Phone: (865) 946-1207

Email: toopstj@ornl.gov

DOE Technology Development Manager:
Kevin Stork

emissions control strategy for controlling NO_x from a lean burn engine running on oxygenated biofuels

- Demonstrated improved NO_x conversion, reduced fuel penalty, and reduced hydrocarbon (HC) slip when using E85 (85% ethanol, 15% gasoline blend) to reduce NO_x with a relatively low cost silver alumina (2% Ag/Al₂O₃) HC SCR catalyst in conjunction with a downstream Cu-exchanged zeolite NH₃ SCR catalyst as compared to the same silver alumina catalyst alone
- Published manuscripts in Applied Catalysis B: Environmental and Catalysis Today on alcohol–gasoline blends with a range of silver alumina catalysts
- Reported primary findings on the impact of trace metals in biodiesel in heavy-duty emissions control systems; presentations given at the 2015 Biodiesel Technical workshop, 10th International Congress on Catalysis and Automotive Pollution Control (CAPoC10), 9th International Conference on Environmental Catalysis, and SAE 2016 International Powertrains, Fuels & Lubricants Meeting; findings were reported in SAE International Journal of Fuels and Lubricants. A book chapter summarizing all of our recent efforts on this subject was also prepared and submitted to Royal Society of Chemistry, Thomas Graham House, Cambridge, UK (*Specialist Periodical Report (SPR) on Catalysis Volume 29*).

Future Directions

- Evaluate light-off temperature reactivity for new Co-Optima fuel candidates and the impact on THC emissions during cold start operation

- Identify emissions control opportunities afforded by Co-Optima fuel candidates
 - Evaluate activity and durability of potential catalyst technologies
 - Identify potential membranes for separating oxygenates from gasoline blends and evaluate separation potential with Co-Optima component blends
- Identify potential impurities in primary Co-Optima fuel component candidates ■

Introduction

The U.S. DOE-funded Co-Optimization of Fuels & Engines effort was established to reduce vehicle petroleum consumption by exploiting the advantageous properties of advanced biofuels to enable more efficient combustion strategies through a co-evolution of engines and fuels. The application of biofuel constituents presents potential opportunities and challenges for meeting emissions regulations with advanced combustion engines. Efforts are focused on identifying unique properties of the new constituents that can either aid emissions control technologies or interfere with them. The efforts specifically address barriers that have been identified in the Vehicle Technologies Office's Multi-Year Plan:

- Inadequate data for fuel effects on emissions and emission control systems
- Inadequate data on long-term impacts of fuel 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 flow reactor studies and engine-based experiments to evaluate the compatibility of Co-Optima fuel candidates with emissions control systems and to identify opportunities for alternative emissions control systems that make use of novel fuel chemistry. The synthetic exhaust gas flow reactor systems are designed to offer maximum flexibility to mimic exhaust conditions expected in application and further allow the exploration of the boundary conditions associated with the candidate emissions control systems. Great care has been taken to ensure the results from the flow reactors will correlate well with engine-based studies. The engine-based experiments rely on conventional commercial engines as

well as simple genset-based engines for long-term aging efforts. Additionally, a comprehensive suite of materials characterization tools are employed as necessary to understand the impact of fuels and their trace constituents on the material properties of the emissions control system.

Results

In prior years, this project evaluated the potential for control of NO_x emissions from lean burn gasoline engines running on biofuel blends through the use of a silver/alumina HC SCR catalyst. Operating gasoline engines under lean (excess air) conditions can improve fuel efficiency by 10–20%, but the three-way catalyst technology used for controlling emissions from engines operated with stoichiometric air–fuel ratios cannot reduce NO_x in the presence of excess oxygen. However, prior results from our group and others [1–6] showed that gasoline blends containing high levels of alcohols (such as ethanol or iso-butanol) are very effective at reducing NO_x when injected into lean exhaust mixtures upstream of a silver/alumina catalyst. Interestingly, results from both flow reactor [1–3] and engine [4–8] experiments have shown that some of the NO_x reduced over the silver/alumina catalyst is converted to NH_3 rather than N_2 . This NH_3 production under lean conditions creates the opportunity for a dual SCR approach [5–8] that adds a copper-exchanged zeolite NH_3 -SCR catalyst downstream of the silver/alumina HC SCR catalyst to utilize the NH_3 to increase NO_x conversion efficiencies and/or reduce the amount of fuel required for NO_x reduction. Our experimental efforts during FY 2016 focused on synthetic exhaust gas flow reactor evaluations of the dual SCR strategy using a splash-blended fuel consisting of 85 vol% ethanol and 15 vol% low sulfur Tier 2 certification gasoline (hereafter referred to as E85).

Flow reactor experiments were conducted with a silver/alumina catalyst alone and with the same silver/alumina catalyst in tandem with a commercial copper-exchanged zeolite NH_3 -SCR catalyst. For the dual SCR configuration, the catalyst samples were placed in two different furnaces to mimic a close coupled silver/alumina catalyst and an underfloor copper zeolite catalyst. Both catalysts were hydrothermally degreened prior to experimental evaluations. Initial runs focused on steady-state NO_x conversions over a wide range of catalyst inlet temperatures and E85 feed rates. The amount of fuel injected into the exhaust is a critical parameter for HC SCR systems, as it increases the total fuel consumption for the engine and aftertreatment system (referred to as a fuel penalty), and it often correlates with HC emissions at the tailpipe. To make full use of the NH_3 generated over the silver/alumina catalyst, evaluations of the dual

SCR configuration also included runs in which the E85 feed was cycled on and off. When the E85 feed was on, the NH_3 generated over the silver/alumina catalyst was stored on the downstream copper zeolite. When the E85 feed was switched off, the NH_3 stored on the downstream copper zeolite was used to convert NO_x until it was depleted. Feedback control was used to turn the E85 back on when the NO_x at the outlet of the copper zeolite exceeded a threshold concentration, ensuring that high NO_x conversion efficiencies were maintained throughout the fuel cycling experiments. Fuel on/off cycling experiments were conducted over a range of fuel feed rates and duty cycles in an attempt to find optimal dual SCR system performance.

Figure 1 shows the NO_x conversion efficiency and associated fuel penalty as a function of silver/alumina catalyst inlet temperature for the silver/alumina catalyst under steady-state conditions, the dual SCR system under steady-state conditions, and the dual SCR system during fuel on/off cycles. The points included in Figure 1 were selected to illustrate optimal performance based on the following criteria: (1) NO_x conversion $>98\%$ and lowest fuel penalty, or (2) best NO_x conversion (if all points were $<98\%$ NO_x conversion). For all temperatures evaluated, the dual SCR system demonstrated improved NO_x conversion efficiency at the same or better fuel penalty compared to the silver/alumina catalyst alone. Cycling the fuel on/off over the dual SCR system resulted in lower fuel penalties at comparable NO_x conversion efficiencies for inlet temperatures of $350\text{--}450^\circ\text{C}$. The lower fuel injection rates required to achieve NO_x conversion with the dual SCR system also result in better HC conversions (Figure 2), which will translate to lower HC slip at the tailpipe. A relatively simple and low platinum group metal containing underfloor clean up catalyst would be expected to treat these HC emissions easily under lean conditions.

Aside from reducing the fuel penalty associated with NO_x control, and reducing tailpipe emissions of the criteria pollutants NO_x and HC, the dual SCR system has additional advantages over the silver/alumina catalyst by itself. Figure 3 shows the fraction of incoming NO_x that is converted to NH_3 over the emissions control system. While NH_3 is not a regulated pollutant, emissions control system designers try to minimize its production. The dual SCR system reduces NH_3 slip under steady-state conditions, and virtually eliminates it under fuel cycling. The complete consumption of NH_3 demonstrates that the dual SCR system is operating as designed, using all of the NH_3 produced by the silver/alumina catalyst to reduce NO_x when the fuel is shut off. One of the potential concerns with any HC SCR system is the production of N_2O , a potent greenhouse gas. Figure 4 shows the

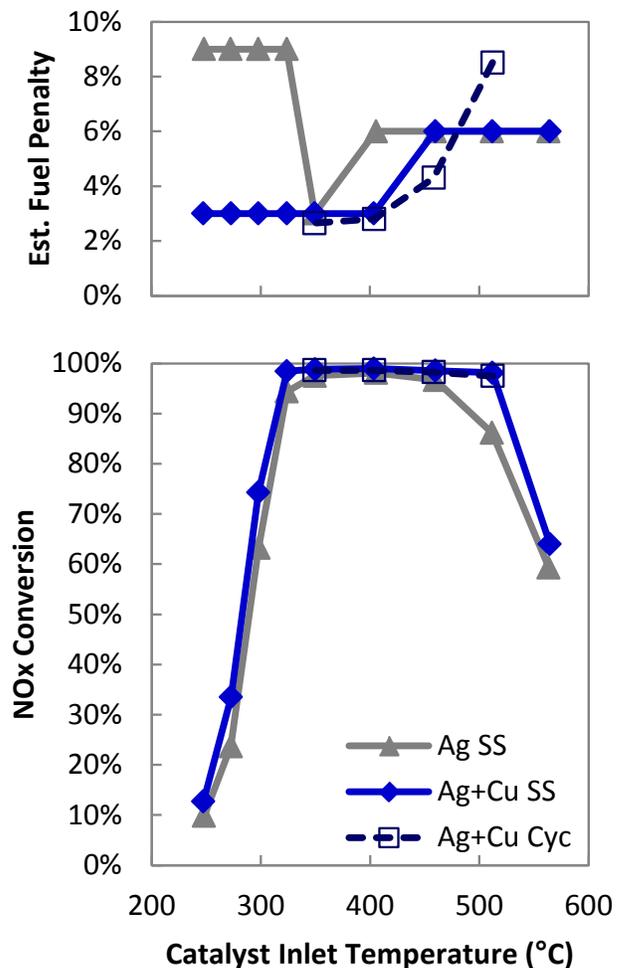


Figure 1. Estimated fuel penalty and NO_x conversion as a function of silver/alumina catalyst inlet temperature for a silver/alumina catalyst at steady-state (Ag SS), a dual SCR system at steady state (Ag+Cu SS), and a dual SCR system under fuel on/off cycles (Ag+Cu Cyc) for synthetic exhaust gas flow reactor experiments conducted with E85

fraction of NO_x converted to N_2O is low for the silver/alumina catalyst, and the dual SCR system reduces N_2O production at low temperatures.

Conclusions

- A dual SCR emissions control system can be an effective strategy for controlling NO_x from a lean burn engine running on alcohol–gasoline blends, such as those under consideration as Co-Optima fuel candidates.
- An optimal on/off cycling of the fuel fed to the dual SCR system further reduces the fuel penalty associated with NO_x reduction and eliminates NH_3 slip.

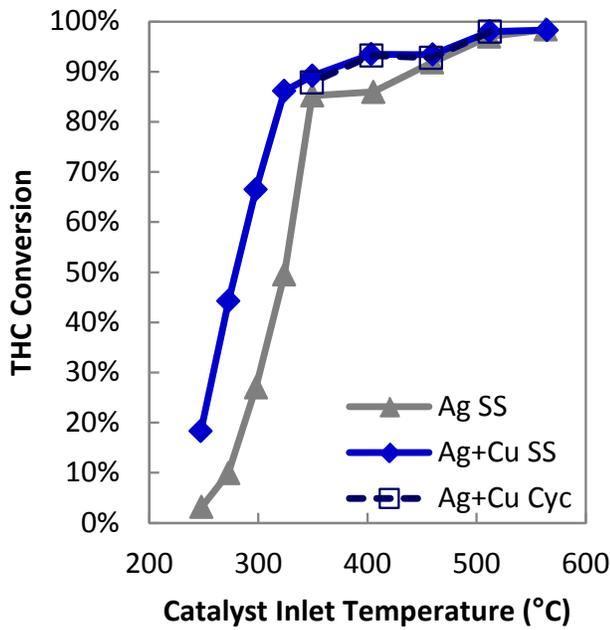


Figure 2. THC conversion as a function of silver/alumina catalyst inlet temperature for a silver/alumina catalyst at steady state (Ag SS), a dual SCR system at steady-state (Ag+Cu SS), and a dual SCR system under fuel on/off cycles (Ag+Cu Cyc) for synthetic exhaust gas flow reactor experiments conducted with E85

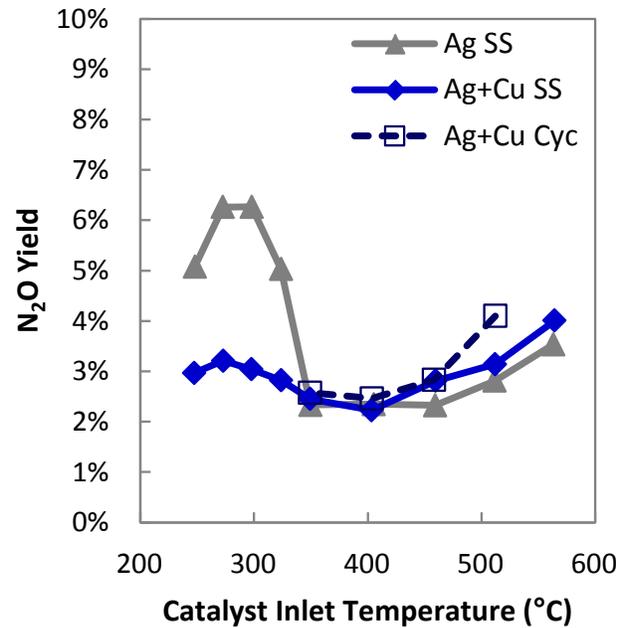


Figure 4. Fraction of inlet NO_x converted to N₂O as a function of silver/alumina catalyst inlet temperature for a silver/alumina catalyst at steady state (Ag SS), a dual SCR system at steady-state (Ag+Cu SS), and a dual SCR system under fuel on/off cycles (Ag+Cu Cyc) for synthetic exhaust gas flow reactor experiments conducted with E85

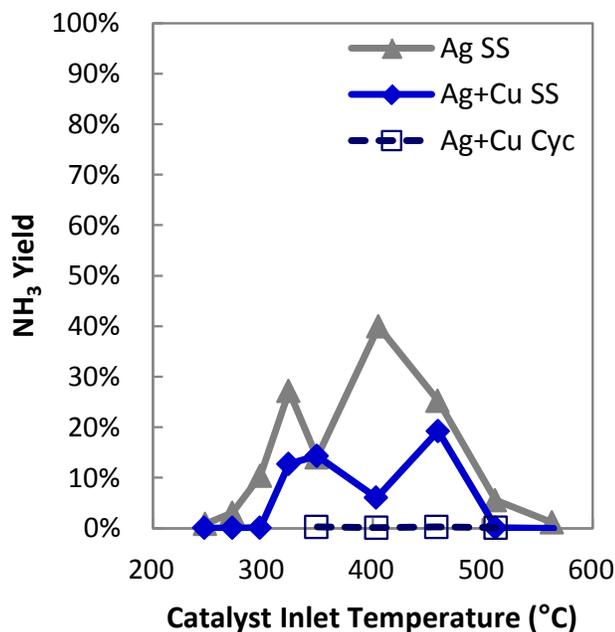


Figure 3. Fraction of inlet NO_x converted to NH₃ as a function of silver/alumina catalyst inlet temperature for a silver/alumina catalyst at steady state (Ag SS), a dual SCR system at steady-state (Ag+Cu SS), and a dual SCR system under fuel on/off cycles (Ag+Cu Cyc) for synthetic exhaust gas flow reactor experiments conducted with E85

- The unique properties of Co-Optima fuel component candidates can be used to access emissions control chemistry that is not achievable with conventional fossil fuels.

References

1. W.L. Johnson II, T.J. Toops, G.B. Fisher, "Mechanistic investigation of ethanol SCR of NO_x over Ag/Al₂O₃," *Catalysis Today* 184 (2012), 166–177; doi:10.1016/j.cattod.2011.12.002.
2. Josh A. Pihl, Todd J. Toops, Galen B. Fisher, Brian H. West, "Selective catalytic reduction of nitric oxide with ethanol/gasoline blends over a silver/alumina catalyst," *Catalysis Today* 231 (2014) 46–55; DOI 10.1016/j.cattod.2013.12.042.
3. Fredrik Gunnarsson, Josh A. Pihl, Todd J. Toops, Magnus Skoglundh, Hanna Härelind, "NO_x conversion over Ag/alumina catalysts via EtOH-SCR using EtOH/gasoline blends," *Applied Catalysis B* 202 (2017) 42–50.
4. 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.
- C. DiMaggio, G. Fisher., K. Rahmoeller and M. Sellnau, SAE J. Fuels Lubr. 2 (2009) 66, also listed as SAE 2009-01-2077.
 - G. Fisher, C. DiMaggio, D. Trytko, K. Rahmoeller and M. Sellnau, SAE Int. J. Fuels Lubr. 2 (2010) 313, also listed as SAE 2009-01-2818.
 - US patent 7,431,905.
 - US patent 7,399,729.
 - D. William Brookshear, Josh A. Pihl, Brian H. West, Todd J. Toops, Vitaly Prikhodko, “The Selective Catalytic Reduction of NO_x over Ag/Al₂O₃ with Isobutanol as the Reductant,” *Catalysis Today* 267 (2016) 65–75.
 - Michael J. Lance, Todd J. Toops, William Brookshear, Andrew A. Wereszczak, Bob McCormick, Adam Ragatz, Richard Ancimer, Hongmei An, Junhui Li, Leigh Rogoski, “Impact of Metal Impurities Present in Biodiesel on Catalyst Durability,” 9th International Conference on Environmental Catalysis, Newcastle, Australia, July 10–13, 2016.
 - (INVITED) Bob McCormick, Aaron Williams, Adam Ragatz, Richard Ancimer, Hongmei An, Leigh Rogoski, Michael Lance, Todd Toops, Andrew A. Wereszczak, “Impact of Metal Impurities on Catalyst Durability,” 2015 Biodiesel Technical Workshop, Kansas City, MO, October 21, 2015.
 - Michael J. Lance, Todd J. Toops, William Brookshear, Andrew A. Wereszczak, William P. Partridge, Bob McCormick, Adam Ragatz, Richard Ancimer, Hongmei An, Junhui Li, Leigh Rogoski, “Impact of Metal Impurities on Catalyst Durability,” 10th International Congress on Catalysis and Automotive Pollution Control (CAPOC10), Brussels, Belgium, October 29, 2015.

FY 2016 Publications/Presentations

- Daniel W. Brookshear, Michael J. Lance, Robert L. McCormick, Todd J. Toops, “Investigations of the Impact of Biodiesel Metal Contaminants on Emissions Control Devices,” *Specialist Periodical Report (SPR) on Catalysis Volume 29*, Royal Society of Chemistry, Thomas Graham House, Cambridge, UK, (2017) Chapter 8, 317–342.
- Fredrik Gunnarsson, Josh A. Pihl, Todd J. Toops, Magnus Skoglundh, Hanna Härelind, “NO_x conversion over Ag/alumina catalysts via EtOH-SCR using EtOH/gasoline blends,” *Applied Catalysis B* 202 (2017) 42–50.
- Michael Lance, Andrew Wereszczak, Todd J. Toops, Richard Ancimer, Hongmei An, Junhui Li, Leigh Rogoski, Petr Sindler, Aaron Williams, Adam Ragatz, Robert L. McCormick, “Evaluation of Fuel-Borne Sodium Effects on a DOC-DPF-SCR Heavy-Duty Engine Emission Control System: Simulation of Full-Useful Life,” *SAE International Journal of Fuels and Lubricants* 9:3 (2016) 683–694; also listed as SAE Technical Paper Series 2016-01-2322.
- Marek Pruski, Aaron D. Sadow, Igor I. Slowing, Christopher L. Marshall, Peter Stair, Jose Rodriguez, Alex Harris, Gabor A. Somorjai, Juergen Biener, Christopher Matranga, Congjun Wang, Joshua A. Schaidle, Gregg T. Beckham, Daniel A. Ruddy, Todd Deutsch, Shaun M. Alia, Chaitanya Narula, Steve Overbury, Todd Toops, R. Morris Bullock, Charles H.F. Peden, Yong Wang, Mark D. Allendorf, Jens Nørskov, Thomas Bligaard, “Virtual Special Issue on Catalysis at the U.S. Department of Energy’s National Laboratories,” *ACS Catalysis* 6 (2016) 3227–3235.

Special Recognitions and Awards/ Patents Issued

- Efforts were part of a team recognized as the 2015 Biodiesel Researchers of the Year in November of 2015. Other members: Bob McCormick (National Renewable Energy Laboratory), Richard Ancimer (Cummins), Michael Lance and Todd Toops (Oak Ridge National Laboratory) for collaborative effort investigating the Impact of Metal Impurities on Catalyst Durability.

II.10 Heat of Vaporization Measurement and Engine Knock Limit Effects

Overall Objectives

The National Renewable Energy Laboratory will clarify the roles and interactions of octane sensitivity (S) and heat of vaporization (HOV) on the knock resistance of high-octane fuels in spark ignition engines, including development of improved methods for measurement of HOV.

Fiscal Year (FY) 2016 Objectives

- Further develop a differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) method to measure the HOV to within 2% accuracy for pure compounds with a known literature value
- Develop a DSC-only method to improve accuracy to within 1% for pure compounds which will compliment the DSC/TGA method
- Apply the improved methods to the measurement of full boiling range gasoline samples and blends with various oxygenates
- Test the null hypothesis using a set of designed fuels that at a given S, the effect of HOV on knock resistance is included in S.

FY 2016 Accomplishments

- The DSC/TGA method was improved to obtain $\pm 2\%$ accuracy for most pure component materials. For highly volatile materials such as hexane, we were not able to obtain better than $\pm 3\%$ (an improvement over the initial $>10\%$ error observed).
- A DSC method was developed in which greater accuracy was achieved relative to the DSC/TGA method. This is because of the higher sensitivity heat flow measurement in the DSC. We observed highly accurate results for many pure components, but again had issues with highly volatile compounds. Additional improvements will be the focus of work in FY 2017.
- Research on fuel knock resistance in a single-cylinder gasoline direct-injection (DI) engine revealed a clear effect of HOV on performance. At retarded combustion phasing and intake air temperatures (IAT) above 60°C , fuels with higher HOV enabled operation at significantly higher loads, i.e., showed improved knock resistance. This suggests that high-HOV fuels

Gina Fioroni (Primary Contact), Matthew Ratcliff, and Robert L. McCormick

National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-4475
Email: gina.fioroni@nrel.gov

DOE Technology Development Manager:
Kevin Stork

may improve fuel efficiency over real-world vehicle operating cycles by reducing the need for spark retard, fuel enrichment, and/or downshifting.

Future Directions

- Gain detailed information on how chemical composition affects instantaneous HOV, we will couple the DSC/TGA instrument to a high-resolution mass spectrometer. This will allow us to not only look at the heat evolved over time (partial HOV), but also to correlate the heat evolved with the species that are being evaporated at any given time in the evaporation curve.
- Further improve the DSC method to achieve better accuracy of pure components, especially those with high volatility. We also plan to extend the method to full boiling range gasoline samples and blends with various oxygenates.
- Perform additional engine experiments at 90°C IAT with isoctane and the E25 fuel to complete the full analysis of these findings. In addition, we plan to extend the study with fuels having higher S (≈ 15) and lower S (≈ 6) than the present range of 11–12. ■

Introduction

HOV is a key fuel property in DI engines, affecting knock resistance, volumetric efficiency, and other factors. Development of a rapid and accurate method to measure the HOV of fuel blends is therefore essential. In prior research, we have developed methods for measuring total HOV of full boiling range gasolines [1]; here we present

work on improved methods. We are also working to develop improved measurements of instantaneous HOV at discrete points in the fraction-evaporated curve to have an improved understanding of how HOV impacts engine operation.

Studies have shown that the effects of ethanol's high HOV on gasoline's knock resistance are included in the Research Octane Number (RON) measurements up to approximately 30% ethanol (E30) blend level [2]. Foong et al. also showed that at the E30 blend level the intake mixture temperature was approximately 25°C for the RON test (compared to 36°C–38°C for E0 gasoline) [2]. It is also known for the Motor Octane Number (MON) test that fuel HOV effects are substantially neutralized because the intake mixture temperature is controlled to a minimum of 141°C [3], which is above the boiling point of ethanol and many gasoline hydrocarbons. The effects of HOV on knock resistance between these intake mixture temperature extremes are not well understood, which provides part of the motivation for this study. Other motivation comes from the recent study by Sluder et al. [4] that suggests the effects of HOV are included in a fuel's octane sensitivity value ($S = \text{RON} - \text{MON}$).

Approach

The analytical instruments used for the HOV measurement part of this study were a DSC and a combined DSC/TGA, both manufactured by TA Instruments. Samples were run in various sample pan and lid configurations. The samples were held at ambient temperature and were allowed to evaporate under a stream of nitrogen gas. The heat flow (and the mass loss for the DSC/TGA) versus time was recorded, and the HOV was calculated by taking the cumulative heat flow and dividing by the sample mass. Calibration procedures are presented in Chupka et al. [1]. Several pure compounds and full boiling range gasoline samples were analyzed.

The engine used for this study was the National Renewable Energy Laboratory's single-cylinder engine, which is based on a production General Motors 2.0-L LNF turbocharged gasoline DI engine. The single-cylinder engine was modified with an additional fuel injector far upstream of the intake port and supplemental intake heating to ensure fuel evaporation while retaining the factory direct injector in-cylinder. Engine specifications and details of this research platform have previously been published [5,6].

Two types of engine experiments were performed. The first type was load sweeps (at a fixed IAT of 50°C) from 7 bar to 19 bar net mean effective pressure (NMEP), beginning with maximum brake torque (MBT) spark

timing, then retarding the combustion phasing as necessary to control knock. Load sweeps spanned a range of K (an empirical engine factor used in calculating octane index) for the engine estimated to be 0.25 to -0.25. The second type involved determination of knock-limited loads as functions of IAT (spanning 35°C to 90°C) for two operating conditions: (1) optimum combustion phasing or MBT spark timing, and (2) at late combustion phasing. Additionally, all experiments were performed using both DI and upstream injection (UI) modes of fueling to determine the effects of evaporative cooling from a given fuel's HOV on knock-limited performance. In the UI mode, the fuel is prevaporized before entering combustion chamber, thus neutralizing the charge cooling that occurs when fuel is injected directly into the cylinder. Knock limits were based on a knock integral (KI) calculation, equal to 10 for the load sweeps and the portion of the IAT study at MBT spark timing. A lower KI of 8 was used for the portion of the IAT study that used late combustion phasing to stay within the maximum cylinder pressure limit of the engine.

Results

HOV Measurement

Table 1 shows HOV values for several pure compounds measured by DSC/TGA. As noted, the error expressed as percent difference from literature values [7] ranges from 5% to well over 10%. Switching to platinum sample pans with increased thermal conductivity and using lids with a laser-drilled pinhole versus screens leads to the improved results shown in Table 2. For materials with vapor pressures at 20°C of less than 6 kPa, accuracy is improved to within 1% or even better. For highly volatile materials, the accuracy was $\pm 5\%$, likely because the very high heat flow required to match their very high rate of evaporation was beyond the capability of this DSC instrument to accurately measure. An improvement was made by switching to lids with no pinhole to slow down the evaporation rate, which improved the measurement to within $\pm 3\%$. It was also observed that during measurements on very low volatility materials that have a slow evaporation rate, the instrument baseline would drift significantly over the several-hour course of the experiment. These measurements could be improved by using no pan lid and reducing the sample size. This suggests a preliminary measurement should be made to determine if the evaporation rate is in the optimal range using a lid with a pinhole, and then a final measurement should be made using an appropriate technique.

A standalone DSC instrument (without TGA capability) can provide a more accurate measure of the heat flow and could potentially provide a more accurate total

Table 1. Measurement of HOV of Pure Compounds by DSC/TGA Using “Old” Method

Compound	Literature Value	Measured Value	% Error
Toluene	412	450.4	9.3
Ethanol	924	1,033.3	11.8
Isooctane	308	323.2	4.9
Hexane	365	405.7	10.8

HOV value due to the better thermocouple design in the instrument. The drawback of this measurement is that the mass loss information is lost from the TGA and therefore the HOV versus fraction evaporated cannot be calculated using this method. Table 3 shows the results for pure compounds measured by the standalone DSC. For most pure compounds, we are within $\pm 1.5\%$ of the literature value, which is in line with the DSC/TGA measurement. The errors for highly volatile compounds are similar to those observed for the measurements using DSC/TGA even with the improved sensitivity of the DSC instrument. Additional method improvements will be the focus of FY 2017.

Engine Studies

The test fuel matrix is shown in Table 4. Its central focus was on fuels having 100 RON and $S \approx 11$, but spans a wide range of HOVs—from 390 kJ/kg to 595 kJ/kg. Renewable oxygenates were blended into gasoline surrogates based on toluene, isooctane, and n-heptane,

Table 3. Measurement of HOVs of Pure Compound by DSC Only

Compound	HOV	Literature Value	% Error
Isooctane	311.0	308	1.0
Toluene	406.5	408	-1.6
Heptane	358.1	360	-0.6
Hexane	381.4	366	4.3

designated here as toluene research fuels (TRFs) plus the RON of the surrogate (e.g., TRF88 had a RON of 88). These surrogate gasolines were used to facilitate designing the blends to the target fuel properties using literature studies by Foong et al. [8] and Morgan et al. [9], as well as oxygenate blending octane number data developed at the National Renewable Energy Laboratory. The designs of the two binary oxygenate blends (E20 +2% p-cresol and E20 +6% anisole) build on results from previous studies of drop-in gasoline fuels by Ratcliff et al. [6] and McCormick et al. [10]. The beneficial effects of high S on knock-limited engine performance, as predicted by Kalghatgi’s Octane Index = $RON - K \cdot S$ [11], were confirmed and benchmarked by comparison with isooctane’s ($S = 0$) performance. Comparison with the performance from a full boiling range gasoline–ethanol blend having 106 RON provided another benchmark for the study.

Figure 1 shows results from DI load sweeps versus the 50% mass fraction burned (CA50) metric for combustion phasing with the seven fuels. The performance benefit

Table 2. Measurement of HOV of Pure Compounds by DSC/TGA Using Improved Method

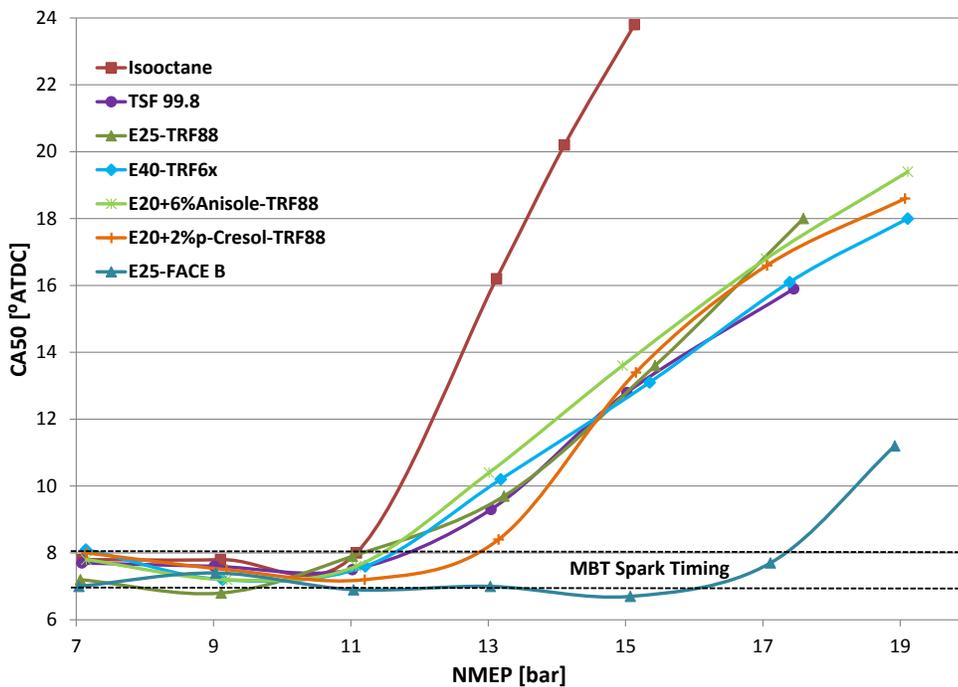
Compound	Literature Value	Measured Value	% Error	Vapor Pressure at 20°C (kPa)
Toluene	413	408	1.2	2.3
Ethanol	924	928	0.4	5.95
Isooctane	308	307	0.3	5.10
Hexane	366	384	4.9	17.6
Hexane*	366	375	2.7	17.6
2-Methylpentane	347	362	4.3	22.0

*Measured using a pan lid without laser-drilled hole.

Table 4. Fuel Matrix for Load Sweep and IAT Studies

Fuel	RON	S	HOV (kJ/kg)	Oxygenate (wt%)
Isooctane (PRF 100)	100	0	303	0
TSF99.8 (74% Tol. in PRF 38.5)	99.8	11.1	390	0
E25 in TRF88 (30% Tol. in PRF 70)	101.6	10.7	489	24.6
E40 in TRF6x (40% Tol. in PRF 32)	99.2	12.2	595	40.3
E20 + 2% p-Cresol in TRF88	101.7	9.4	472	22.4
E20 + 6% Anisole in TRF88	99.9	9.6	472	26.5
E25- FACE B	105.6	11.8	485	26.3

FACE-B= a standard gasoline developed by the Coordinating Research Council
 PRF = primary reference fuel
 TSF = toluene standardization fuel



ATDC - after top dead center

Figure 1. Direct injection load sweeps versus 50% mass fraction burned (CA50) combustion phasing at IAT = 50°C. MBT combustion phasing was maintained up to the knock limit (KI = 10) and then spark timing was retarded to maintain this value of KI as load was increased.

from fuels with $S \approx 11$ compared with isooctane ($S = 0$) is clear. For example, a load of 15-bar NMEP was effectively the highest output for isooctane because nearly 17 degrees of spark retard (relative to MBT spark timing) was required to control knock. The resulting late

combustion phasing at CA50 $\approx 24^\circ$ after top dead center was beginning to cause combustion instability. In contrast, only six degrees of spark retard was required to control knock for the high S fuels at 15 bar NMEP, providing access to 4 bar higher NMEP using additional spark

retard. Minimizing combustion phasing retard implies higher thermal efficiency because the phasing is closer to optimal (i.e., MBT). Note that even higher loads might be achieved from the high S fuels by retarding combustion phasing further. However, an upper NMEP limit of 19 bar has been imposed on the experimental protocol, because this load corresponds with peak cylinder pressures at or near General Motor's recommended limit of 100 bar.

The overall performance benefit of high S at 100 RON is less than that observed by increasing RON from 100 to 106 (see the curve for E25-FACE B), which allowed MBT phasing to 17 bar NMEP. However, above approximately 11 bar NMEP more than half the benefit of the 106 RON fuel (relative to isooctane S = 0) is provided by the S \approx 11 fuels. The five high-S fuels all provide essentially the same performance, within experimental error. Thus, in this experiment knock-limited performance appears to be independent of the fuels' HOV, suggesting that HOV effects are included in S under these operating conditions.

Figure 2 shows knock-limited results from the IAT dependency study at late combustion phasing. As shown in Figure 1, the high values of NMEP in Figure 2 require significant spark retard. Figure 2 shows the significant advantage for DI versus UI for all fuels at all IAT values in terms of higher achievable load at fixed combustion phasing. This is a direct effect of evaporative cooling of the fuel-air charge in the DI case. The knock-limited performance of isooctane using DI was significantly

lower than performance of the high-S fuels using UI, underscoring the performance benefits of the high S fuels shown by the DI load sweeps in Figure 1.

The DI data (solid lines) indicate that the high-HOV fuels E20 +2% p-cresol (472 kJ/kg) and E40 (595 kJ/kg) have performance advantages over the equivalent RON and S TSF99.8 (390 kJ/kg) at IATs greater than 50°C. The performance improvement was largest at 90°C, which was larger for E40 than for E20 +2% p-cresol, suggesting that the effect arises from these fuel's higher HOVs (see HOV data in Table 4). Prior work conducted in collaboration with Oak Ridge National Laboratory demonstrated that at lower IAT, HOV is captured in the RON measurement [4], and can be thought of as a component of S. At higher IAT, this work shows that HOV has a measureable effect on knock resistance independent of S. IATs at $\geq 60^\circ\text{C}$ are above that used in the RON test and can occur after hot soak or at low vehicle speeds in high ambient air temperature conditions.

Conclusions

- An improved DSC/TGA method was developed to measure the HOV of pure components to within a $\pm 1\%$ error for most pure compounds except those that are highly volatile. Additional method improvements are being investigated to improve measurement accuracy for highly volatile compounds.

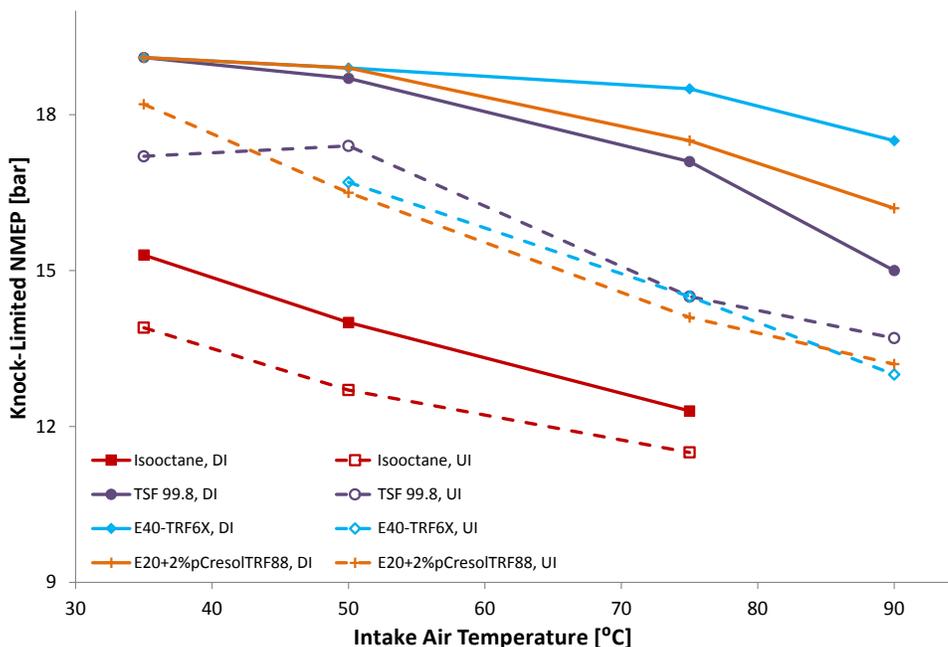


Figure 2. Knock-limited (KI = 8 for these experiments) performance at late combustion phasing as a function of IAT and fueling mode

- An initial DSC method was developed to measure the HOV of pure compounds and will be applied to full boiling range gasoline samples in FY 2017.
 - Based on the load sweep results at an IAT of 50°C, the effect of HOV on knock resistance appears to be included in S, i.e., five fuels having $S \approx 11$ but with HOVs ranging from 390–595 kJ/kg gave identical results within experimental error.
 - The performance benefit of high-S fuels was clearly demonstrated above an NMEP of 11 bar in the load sweep experiments, where fuels with $S \approx 11$ provided roughly half the benefit of 106 RON fuel, relative to isooctane ($S = 0$). This advantage was highlighted in the IAT sweeps where the high-S fuels injected in UI mode provided better performance than isooctane in DI mode.
 - The IAT sweeps in DI mode revealed a clear positive effect of HOV on performance. At retarded combustion phasing and IATs above 60°C, fuels with higher HOV enabled operation at significantly higher loads. This observation suggests that high-HOV fuels may improve fuel efficiency over real-world vehicle operating cycles by reducing the need for spark retard, fuel enrichment, and/or downshifting to maintain load at high ambient temperatures.
6. 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.” *SAE Int. J. Fuels Lubr.* 9(1):59–70, 2016, doi:10.4271/2016-01-0705.
 7. Chickos, J.S., and Acree, W.E. “Enthalpies of Vaporization of Organic and Organometallic Compounds, 1880–2002.” *J. Phys. Chem. Ref. Data* 32:519–878, 2003.
 8. Foong, T.M., Morganti, K.J., Brear, M.J., da Silva, G., Yang, Y., Dryer, F.L. “The Octane Numbers of Ethanol Blended with Gasoline and its Surrogates.” *Fuel* 115:727–739, 2014.
 9. Morgan, N., Smallbone, A., Bhawe, A., Kraft, M., Cracknell, R., Kalghatgi, G. “Mapping Surrogate Gasoline Compositions into RON/MON Space.” *Combustion and Flame* 157: 1122–1131, 2010.
 10. McCormick, R.L., Ratcliff, M.A., Christensen, E., Fouts, L., Luecke, J., Chupka, G.M., Yanowitz, J., Tian, M., Boot, M. “Properties of Oxygenates Found in Upgraded Biomass Pyrolysis Oil as Components of Spark and Compression Ignition Engine Fuels.” *Energy Fuels*, 29(4):2453–2461, 2015.
 11. Kalghatgi, G., “Fuel Anti-Knock Quality – Part II, Vehicle Studies – How Relevant is Motor Octane Number (MON) in Modern Engines.” SAE Technical Paper 2001-01-3585, 2001. doi:10.4271/2001-01-3585.

References

1. Chupka, G.M., Christensen, E., Fouts, L., Alleman, T.L., Ratcliff, M., McCormick, R.L. “Heat of Vaporization Measurements for Ethanol Blends Up To 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines.” *SAE Int. J. Fuels Lubr.* 2015, doi:10.4271/2015-01-0763.
2. Foong, T., Morganti, K., Brear, M., da Silva, G., et al. “The Effect of Charge Cooling on the RON of Ethanol/Gasoline Blends.” *SAE Int. J. Fuels Lubr.* 2013; 6(1), doi:10.4271/2013-01-0886.
3. ASTM International. ASTM D2700-16, Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel. 2016.
4. Sluder, C.S., Szybist, J.P., Ratliff, M., McCormick, R.L., Zigler, B.T. “Exploring the Relationship between Fuel Heat-of-Vaporization and Sensitivity.” *SAE Int. J. Fuels Lubr.* 9(1):80–90, 2016, doi:10.4271/2016-01-0836.
5. He, X., Ratcliff, M.A., and Zigler, B.T., “Effects of Gasoline Direct Injection Engine Operating Parameters on Particle Number Emissions.” *Energy Fuels* 26:2014–2027, 2012.

FY 2016 Publications/Presentations

1. Sluder, C.S., Szybist, J.P., Ratliff, M., McCormick, R.L., Zigler, B.T. “Exploring the Relationship between Fuel Heat-of-Vaporization and Sensitivity.” *SAE Int. J. Fuels Lubr.* 9(1):80–90, 2016, doi:10.4271/2016-01-0836.
2. McCormick, R.L., Fioroni, F., Szybist, J., Bays, T., Miles, P., McNenly, M., Pitz, W., Luecke, J., Ratcliff, M., Zigler, B., Goldsborough, S. “Co-Optimization of Fuels and Engines Fuel Property Team: Part 1 - Fuel Properties and Chemical Kinetics.” Presented at Vehicle Technologies Office Annual Merit Review, June 9, 2016.
3. Szybist, J., Sluder, S., Ratcliff, M., Wallner, T., Splitter, D., Ickes, A., Kolodziej, C.P., McCormick, R., Miles, P. “Co-Optimization of Fuels and Engines Fuel Property and Advanced Engine Development Team: Thrust I engine projects.” Presented at Vehicle Technologies Office Annual Merit Review, June 9, 2016.

4. McCormick, R.L. "Co-Optimization of Spark-Ignition Engines and Biofuels." Presented at Colorado State University, April 19, 2016.
5. McCormick, R.L. "High Octane Fuels: Benefits and Challenges." Presented at Clean Cities Coordinator Webinar, March 17, 2016.
6. McCormick, R.L. "Co-Optimization of Internal Combustion Engines and Biofuels." Presented at Future Fuels Workshop, King Abdullah University of Science and Technology, Saudi Arabia, March 8, 2016.
7. McCormick, R.L. "High Octane Fuels: Benefits and Challenges." Presented at National Ethanol Conference, New Orleans, LA, February 17, 2016.

III. Co-Optimization of Fuels and Engines: Medium/Heavy-Duty

Research efforts in this area are exploring the factors important for enabling advanced compression ignition engine technologies, which are most applicable to medium- and heavy-duty vehicles. Engine and fuels performance research has been integrated to identify fuel properties that critically impact kinetically controlled combustion and low-temperature combustion for high efficiency with low emissions.

III.1 Investigation on the Combustion of Selected High RON (Co-Optima) Fuels under GCI Operating Conditions

Overall Objectives

- Demonstrate adapted engine operation (1.9-L General Motors) on high octane fuels (aromatic, alkylate, E30 [30% ethanol, 70% gasoline blend]) for Co-Optima using an advanced combustion concept, gasoline compression ignition (GCI)
- Achieve a desirable engine output (emission, noise, efficiency) using different GCI operating strategies at different engine speeds and loads
- Investigate through engine experiment on combustion and emission behavior of the fuels under a low temperature combustion (LTC) condition that could be related to fuel properties (i.e., heat of vaporization, sensitivity or RON-MON, where RON = Research Octane Number, MON = Motor Octane Number)

Fiscal Year (FY) 2016 Objectives

- Establish GCI engine operating strategy to compensate for the high resistance to auto-ignition of high RON fuels
- Investigate the effect of various parameters (temperature, boost, dilution, start of injection [SOI]) on engine performance and emission of each fuel
- Demonstrate a desirable engine output (emission, noise, efficiency) with GCI operation at low and intermediate loads

FY 2016 Accomplishments

- Developed GCI engine operating strategy to achieve a stable (coefficient of variation in indicated mean effective pressure <3%), relatively low noise (~85 dB), low emission (hydrocarbon [HC], CO < 5 g/kW-hr) and soot (<0.1) for all high RON fuels at intermediate load (3–6 bar brake mean effective pressure [BMEP])
- Quantified dilution limit (utilize low pressure exhaust gas recirculation [EGR] with maximum 30% EGR for stable combustion) for different global equivalence ratio conditions (1.6–2.0) at a given engine operating condition (constant combustion phasing ~5° after top dead center [aTDC])
- Investigated the sensitivity on combustion phasing as boost and temperature are changed simultaneously and the corresponding effect on autoignition (assessment of

Stephen Ciatti

Argonne National Laboratory (ANL)
9700 Cass Avenue
Lemont, IL 60439
Phone: (630) 252-5635
Email: sciatti@anl.gov

DOE Technology Development Manager:
Kevin Stork

low temperature heat release, intermediate temperature heat release).

- Captured endoscope images to visualize the spray/combustion for various conditions: flame development of first and second injections; soot radiation comparison for different fuels (E30 showed lowest soot volume fraction levels)

Future Directions

- Continue exploring different engine speed and load (higher) that can be achieved with desirable engine outputs (soot, emission, noise, efficiency) under LTC condition
- Provide engine conditions and data (cylinder pressure, emission, endoscope images) for computational fluid dynamics modeling (ANL – Sibendu) to have simulations that can provide more insights on in-cylinder combustion process
- Correlate with CFR data to characterize the effect of heat of evaporation of the fuels on auto-ignition and noise
- Investigate the correlation of P–T sensitivity, and fuel stratification between advanced compression ignition engine and rapid compression machine data (ANL – Goldsborough) to better understand the autoignition behavior of different high RON fuels
- Obtain general characteristics of particulate matter (PM) through transmission electron microscope sampling (ANL – Seungmok) for these fuels with very different aromatic content or PM index under compression ignition condition ■

Introduction

Improvement in emission and engine efficiency has been achieved through utilization of the LTC concept for advanced combustion engines such as GCI [1–4] and reactivity controlled compression ignition [5]. Understanding the physical (mixing, evaporation) and chemical (reactions that lead to the autoignition and heat release of fuel) processes is the fundamental key to achieve engine operating strategies to a specific engine platform and fuel. The use of fuel injection pressure, number of injections, split ratio (pilot and main), SOI, and injector nozzle design provides a platform of local fuel richness distribution (homogenous to fully stratified) within the cylinder prior and during the combustion process. Meanwhile, other parameters such as EGR, intake temperature, and boost can alter the chemical pathway that leads to the auto-ignition and the consequent emissions and soot. Utilization of both injection strategy and other engine conditions (i.e., EGR) can result into a desirable engine output: low emissions, low Filter Smoke Number (FSN), minimum combustion noise, and highly efficient engine performance. Physical and chemical properties of the fuel and conventional fuel metrics characterized by RON and MON values are examples of the most important factors that dictate the autoignition and emissions phenomenon.

Under the GCI operating condition, early injection of gasoline fuel (higher resistance to autoignition than diesel) can provide a sufficient mixing time, hence avoiding the fuel-rich region that can result in high smoke emissions. Fuels with a high octane number tend to have more resistance to autoignition. Therefore, if not operating properly, a high pressure rise rate can occur as most of the injected fuel can burn simultaneously, which is often known as noise challenge in homogeneous charge compression ignition engines for high load [6]. Moderate fuel stratification seems to facilitate the noise issue (mostly premixed combustion) and smoke problem (diffusion flame) [7]. Moderate fuel stratification is achieved through multiple injections with one relatively early injection of the pilot and near-top dead center injection of the main. High combustion efficiency is achieved for low-intermediate load with low emissions of HC and CO. A moderate EGR level of 25% has been shown to be sufficient to reduce thermal NO_x emissions caused by high combustion temperature and delay the combustion phasing at high load.

Approach

The current work is focused on addressing the engine strategy to operate high RON fuels using a GCI approach

on a multi-cylinder engine. The varied parameters for engine operation include SOI, global equivalence ratio, EGR, temperature, and boost. Each fuel (aromatic, alkylate, E30) is tested in a 1.9-L General Motors engine at ANL. Engine data (cylinder pressure, heat release rate [HRR], etc.), emissions (NO_x , HC, CO), PM measurement (transmission electron microscope sampling), and endoscope images were collected to quantify the effect of given parameters. Possible correlation between measurement approaches can provide deeper insights on the fuel dependence or parametric effect on engine performance. Most of the tested conditions were taken with consideration for practical requirements for noise (below 90 dB for 6 bar BMEP) and FSN (<0.1 for most cases). The engine is equipped with a supercharger (Eaton) that delivers a precisely controlled boost pressure. Meanwhile, EGR is delivered through a low pressure, cooled, particulate filter loop by a number of valves and throttle. The injection system consists of a Bosch common rail with a belt-driven CPIH pump that provides high fuel pressure (maximum of 1,600 bar) to seven-hole injectors. Engine emissions were collected via an AVL AMA i60. Smoke was measured by an AVL 415S smoke meter.

Multiple GCI strategies were applied at LTC conditions to operate high RON gasoline fuels initially for a stable combustion (coefficient of variation in indicated mean effective pressure $< 3\%$), and low combustion noise with relatively low emission and soot. It was shown that at an engine speed of 1,000 rpm with double injection strategy, all of these fuels can be run reasonably well up to an engine load of 6 bar BMEP. Combustion phasing was kept constant at 5° aTDC ($\pm 1^\circ$). This was done purposely to maintain a relatively low combustion noise, and to sustain the combustion while running a highly diluted condition ($\sim 30\%$ EGR). Later combustion phasing may be needed in future tests for handling noise at a higher engine load and speed (i.e., 8 bar BMEP or higher). A test matrix was then generated to perform a study on the effect of multiple parameters on ignition, combustion phasing, and emissions of each individual fuel. As summarized in Table 1, these parameters are EGR, SOI of main injection, inlet temperature, boost pressure, and global lambda. HRR profiles were used to show the difference in combustion behavior of each fuel where low-intermediate heat release can be seen. Emissions (NO_x , HC, CO) and FSN measurement were taken for different global lambda ($\lambda = 1.6, 1.8, 2.0$) and EGR level (0–30%). Through this approach, the effects of fuel stratification and dilution can be obtained separately to describe their sensitivity on each fuel. As EGR is increased, SOI of the main injection or intake pressure was adjusted accordingly so that combustion phasing stayed constant. Therefore, the reactivity of the fuel can be controlled by either the

Table 1. Baseline Operating Conditions

Parameter	Value
Engine 1.9-L GM 4-cylinder (17.8:1 CR)	
Engine Speed [rpm]	1,000
Engine Load [bar BMEP]	3–6
Fuel – 98 RON	Aromatic, Alkylate, E30
Injection Pressure [bar]	600
Start of Injection [°aTDC]	-50/varied
Fuel Split (~ % by duration)	55/45
EGR [%]	0–30
Boost Pressure [bar(a)]	1.4
Intake Air Temp [°C]	55
Global λ (= 1/ Φ)	1.8

CR – compression ratio

local equivalence ratio (mixing time increases for early injection) or autoignition influenced by boost. With fixed SOIs of pilot and main, the reactivity of the fuels was controlled by adjusting simultaneously intake temperature and boost. Finally, endoscope images were obtained for all three fuels for an EGR sweep from -5° aTDC to 30° aTDC capturing the entire visible combustion process event.

Results

At each different global lambda, the smoke number reduced as EGR increased for all fuels as shown in Figure 1 (left). The highest smoke number resulted from the combustion of aromatic fuel, while combustion of E30 resulted with the lowest FSN. With EGR >20% and lambda of 1.8, E30 and alkylate give an FSN below 0.1. For lambda of 2.0, the combustion was lean enough that the FSN is below 0.1 for all fuels at any given EGR (0–30%). High FSN (>0.5) is seen when operating at lambda of 1.6. However, it seems that with EGR of greater than 25%, FSN can be managed to be very low (<0.1). It was not possible to run lean and highly diluted condition as the combustion starts to diminish due to low reactivity from lack of fuel stratification and oxygen. In Figure 1 (right), NO_x , HC, and CO from the combustion of aromatic fuel were relatively low (<5 g/kW-hr) with NO_x being lowest at 10% EGR. CO tends to increase with EGR of 25% or higher.

Combustion efficiency was very high (>99.9%) for all conditions as shown in Figure 2. Noise level was below 90 dB for most of the cases. At ~5.5 bar BMEP, noise was kept at nearly 85 dB when running at lambda of 1.6 and 20% EGR with proper injection time of the main injection. While CA50 (crank angle for 50% burn) is kept constant, increasing EGR delayed the autoignition of the fuels with later CA10 as shown in Figure 3 (left). The HRR curves for three fuels at 20% EGR show some low temperature combustion for E30 and alkylate before

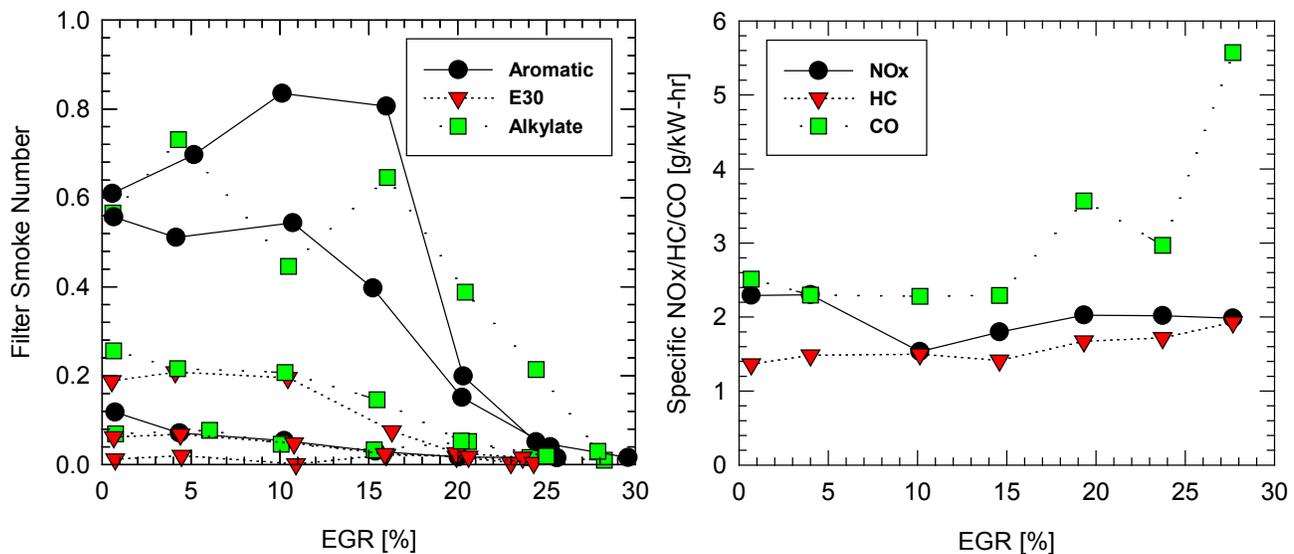


Figure 1. Left: Effect of EGR and global lambda on smoke emission of 98 RON fuels (aromatic, E30, alkylate). Right: Sample emissions (NO_x , HC, and CO) from combustion of aromatic at different EGR levels for a constant global lambda.

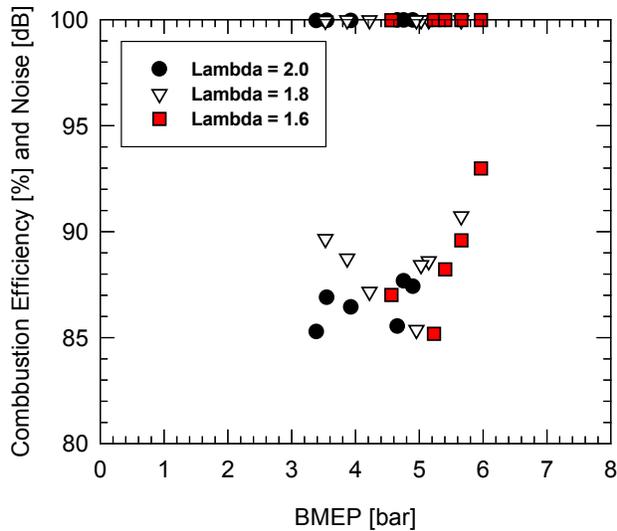


Figure 2. Sample of combustion efficiency and noise for tested engine loads of aromatic at different λ (2.0, 1.8, and 1.6)

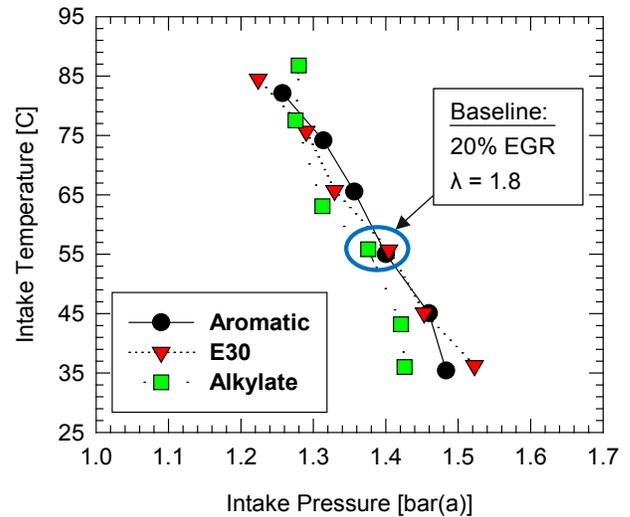
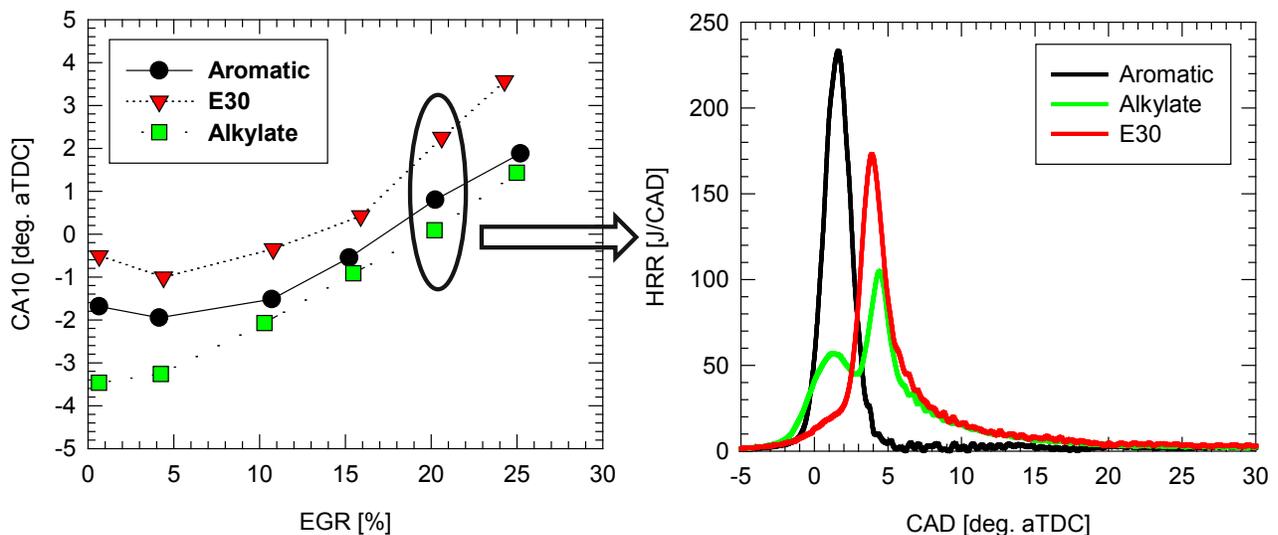


Figure 4. Sensitivity of boost and intake temperature on combustion phasing of three fuels (aromatic, E30, alkylate) at fixed condition (20% EGR, $\lambda = 1.8$)

maximum HRR. This was not seen in combustion of aromatic. In Figure 4, with the same intake temperature range varied from 35°C to 85°C, the smallest boost range of 1.27–1.43 bara was used for constant combustion phasing of alkylate. E30 has the least boost sensitivity with the largest boost range from 1.22–1.52 bara.

Several selected time-elapsd endoscope images are shown in Figure 5. In general, a less amount of soot was accumulated on the window when running E30 as compared to alkylate and aromatic. With E30, higher

EGR showed longer delay in the start of combustion on the images; very weak combustion at 3° aTDC for 20% EGR as compared to lower EGR or no EGR cases. The combustion already started at 0° EGR for E30 during the injection of the main. The images showed similarity of combustion process for all three fuels at 20% EGR. Images for alkylate and aromatic are set with a low exposure time of 20 μ s to prevent intensity saturation. E30 has a relatively lower flame intensity compared to the other fuels, therefore the exposure time was increased



CAD – crank angle degrees; CA10 – crank angle for 10% burn

Figure 3. Left: Effect of EGR on autoignition of three fuels (aromatic, E30, alkylate) at baseline condition ($\lambda = 1.8$). Right: HRR of three fuels at 20% EGR.

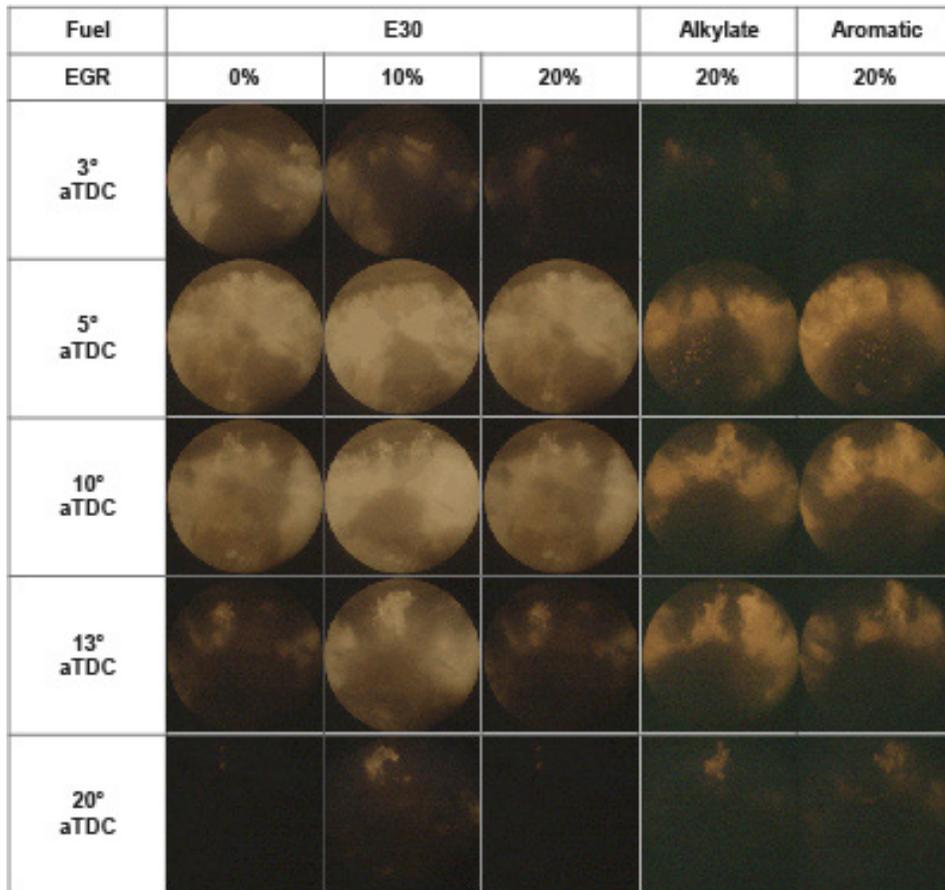


Figure 5. Endoscope images of different fuels (same RON) at various EGR levels ($\lambda = 1.8, T_{in} = 55^\circ\text{C}, P_{in} = 1.4 \text{ bara}$)

to 20 μs . Soot during the combustion process was built up on the window preventing the view of the spray and combustion of alkylate and aromatic even though the nozzle and injector were adjusted to avoid fuel impingement.

Conclusions

- Three fuels (aromatic, alkylate, and E30) with 98 RON were tested in a GCI multi-cylinder engine using a double injection strategy. In general, the combustion was very stable and emissions of soot, NO_x , HC, and CO were low at LTC conditions with moderate EGR levels.
- Combustion noise was kept below 90 dB in all tested loads of 3–6 bar BMEP. This was achieved by maintaining CA50 at 5° aTDC. SOI of the main injection or boost were demonstrated to be effective in controlling the combustion phasing during the EGR sweep. Autoignition or CA10 were, however, retarded as EGR increases with E30 having later ignition than other fuels.

- HRR profiles show some low temperature heat release for all the fuels, but more obvious for E30 and alkylate.
- P–T sensitivity for conditions of 20% EGR and lambda of 1.8 showed that E30 was the least boost sensitive compared to other fuels.
- E30 also produces the lowest combustion intensity as seen in endoscope images. The combustion of aromatic show strong intensity (saturated if keeping the same exposure time as in E30 case), even though measured FSN was low for the same case.

References

1. Ciatti, S., Johnson, M., Adhikary, B.D., Reitz, R.D., & Knock, A., “Efficiency and Emissions Performance of Multizone Stratified Compression Ignition Using Different Octane Fuels,” SAE Technical Paper 2013-01-0263, 2013.
2. Kalghatgi, G., Hildingsson, L., & Johansson, B., “Low NO_x and low smoke operation of a diesel engine using

gasolinelike fuels,” *Journal of Engineering for Gas Turbines and Power*, 132(9), 2010.

3. Manente, V., Zander, C.G., Johansson, B., Tunestal, P., & Cannella, W., “An advanced internal combustion engine concept for low emissions and high efficiency from idle to max load using gasoline partially premixed combustion,” *SAE Technical Paper 2010-01-2198*, 2010.
4. Sellnau, M., Sinnamon, J., Hoyer, K., & Husted, H., “Gasoline direct injection compression ignition (GDICI)-diesel-like efficiency with low CO₂ emissions,” *SAE International Journal of Engines*, 4, (2011-01-1386, 2010-2022, 2011.
5. Kokjohn, S.L., Hanson, R.M., Splitter, D.A., & Reitz, R.D., “Fuel reactivity controlled compression ignition (RCCI): a pathway to controlled high-efficiency clean combustion,” *International Journal of Engine Research*, 12(3), 209-226, 2011.
6. Kalghatgi, G.T., “The outlook for fuels for internal combustion engines,” *International Journal of Engine Research*, 2014.
7. Dempsey, A.B., Curran, S.J., & Wagner, R.M., “A perspective on the range of gasoline compression ignition combustion strategies for high engine efficiency and low NO_x and soot emissions: Effects of in-cylinder fuel stratification,” *International Journal of Engine Research*, 2016.

FY 2016 Publications/Presentations

1. Kodavasal, J., Ciatti, S., & Som, S., “Analysis of the Impact of Uncertainties in Inputs on CFD Predictions of Gasoline Compression Ignition,” *ASME ICEF*, Paper No. ICEF2016-9328, 2016.
2. Cung, K., Rockstroh, T., Ciatti, S., Cannella, W., & Goldsborough, S.S., “Parametric Study of Ignition and Combustion Characteristics from a Gasoline Compression Ignition Engine Using Two Different Reactivity Fuels,” *ASME ICEF*, Paper No. ICEF2016-9395, 2016.
3. Kodavasal, J., Kolodziej, C.P., Ciatti, S.A., & Som, S., “Effects of injection parameters, boost, and swirl ratio on gasoline compression ignition operation at idle and low-load conditions,” *Int. J Engine Res.*, 2016.
4. Kodavasal, J., Pei, Y., Harms, K., Ciatti, S., Wagner, A., Senecal, P., Som, S., “Global Sensitivity Analysis of a Gasoline Compression Ignition Engine Simulation with Multiple Targets on an IBM Blue Gene/Q Supercomputer,” *SAE Technical Paper 2016-01-0602*, 2016.
5. Cung, K., Ciatti, S., “Recent Progress on Advances in High-Efficiency Gasoline Compression Ignition: Investigation of LP-EGR effect on Reduction of Soot, Emission, and Noise,” *AEC Program Review Meeting*, August 16, 2016, USCAR, Southfield, MI, USA.

III.2 Autoignition Fundamentals of Fuels for Boosted SI and LTGC Engines

Overall Objectives

- Provide a fundamental understanding of the autoignition behavior of advanced fuels at operating conditions relevant to boosted spark ignition (SI) and advanced compression ignition (ACI) engines
- Evaluate the Central Fuel Hypothesis and determine fuel properties required to correctly specify fuels for these advanced engines and operating modes
- Provide data for chemical–kinetic model development and validation

Fiscal Year (FY) 2016 Objectives

- Design a test matrix for boosted SI fuels, in collaboration with Oak Ridge National Laboratory (ORNL), to evaluate the Central Fuel Hypothesis for fuels with both low and high of octane sensitivity and for changes in the blending compounds used to produce the high sensitivity
 - Fuels matrix will be used by multiple laboratories within Co-Optima for tests on both boosted-SI and ACI engines
- Establish an engine operation test matrix for evaluating fuel effects on low-temperature gasoline combustion (LTGC) performance; LTGC is a form of ACI
 - Include well-controlled, homogeneous LTGC operation to provide data for evaluating fuel performance related to knock in SI engines, and for evaluating chemical–kinetic models
- Acquire LTGC engine performance data over this engine operation matrix for a high-Research Octane Number (RON), high-sensitivity fuel from the fuels matrix, and for regular grade E10 (10% ethanol, 90% gasoline blend).
- Quantify the differences in autoignition behavior and performance of this high-RON, high-sensitivity fuel compared to regular E10 (Reg-E10).

Accomplishments

- Established initial fuels test matrix in collaboration with ORNL, consisting of three RON 98 fuels, one each with (1) low sensitivity, (2) high-sensitivity with 30%

John E. Dec

Sandia National Laboratories
MS 9053, P.O. Box 969
Livermore, CA 94551-0969
Phone: (925) 294-3269
Email: jedec@sandia.gov

DOE Technology Development Manager:
Kevin Stork

ethanol, and (3) high-sensitivity with high aromatic content

- Acquired all three fuels
- Initiated an expansion of the fuels matrix to include two additional RON 98, high-sensitivity fuels with (1) high-olefin and (2) high-cycloalkane content
 - Working with fuel supplier to obtain these additional fuels
- Established an engine operation test matrix for evaluating fuel effects for LTGC combustion, performance related to knock in SI engines, and to provide data for chemical–kinetic model validation
- Acquired detailed LTGC engine performance data for the RON 98, high-aromatic fuel over the engine operation test matrix
 - Data included measurements of ϕ sensitivity, a key parameter for LTGC and some other ACI concepts (see discussion in the Approach section)
- Acquired similar detailed LTGC performance data for a Reg-E10 gasoline and compared results with the high-aromatic fuel to quantify differences
 - Compared the high-aromatic fuel with data from previous tests with other fuels
- Analyzed these new data and performed an initial assessment of the ability of the Octane Index (OI) to correlate the data from these fuels at naturally aspirated conditions

Future Directions

- Acquire detailed LTGC engine performance data for the other fuels in the fuels test matrix, fuels with (1) low-sensitivity, (2) high-sensitivity with 30% ethanol, (3) high-sensitivity with high-olefin content, and (4) high-sensitivity with high-cycloalkane content
- Analyze data for these four additional fuels and compare performance with that of the two fuel tested in FY 2016
 - Evaluate the performance of the OI for comparing these fuels at both naturally aspirated and intake-boosted conditions
 - Determine the effects of the various components used to achieve RON 98 with high sensitivity in the fuel matrix
- Acquire LTGC performance data for other gasoline-like fuels that have high levels of bio-derived components
- Evaluate these gasoline-like fuels for their potential to work in LTGC engines, including their ϕ -sensitivity
- Work with the High Performance Fuels team to identify bio-fuel components with good potential for blending ACI fuels, and test the performance of these ACI fuels
- Provide data to the Toolkit team for chemical-kinetic model development and evaluation ■

Introduction

Engines using LTGC, which includes homogeneous charge compression ignition (HCCI) and stratified variants of HCCI, have a strong potential to reduce fuel costs for transportation by 30% or more due to their high thermal efficiencies and ultra-low NO_x and particulate emissions. This makes LTGC an important ACI engine concept, and LTGC research engines also provide an excellent platform for determining the autoignition properties of fuels when they are operated in a well-mixed, HCCI mode. As such, they provide a means of evaluating the Central Fuels Hypothesis and determining whether standard autoignition metrics (RON and Motor Octane Number [MON]) are adequate for advanced high-boost engines, or if additional autoignition metrics and specifications will be required. These well-mixed compression ignition data provide autoignition measurements relevant to both boosted SI [1] and ACI concepts. They are also important for validating chemical-kinetic models for the new fuels being developed under Co-Optima.

Approach

A test matrix for boosted SI fuels was designed in collaboration with ORNL to provide an improved understanding regarding two key questions for advanced fuels and engines. First, for high RON fuels, what is the potential benefit of high octane sensitivity ($S = \text{RON} - \text{MON}$)? Second, do all fuels with the same high-RON and high-S values have the same the autoignition/knock performance, or are autoignition/knock also affected by fuel composition? To address these questions, a fuels matrix was developed that consisted of three fuels, one with a high RON = 98 and a low $S = 1$, and two RON = 98 fuels with a high $S \approx 10.5$, but with different constituents for about 30% of the fuel volume as follows: (1) 30% ethanol and (2) high-aromatic content. These three fuels were acquired for our tests and for testing at other laboratories within Co-Optima. An effort was also initiated to expand this fuels matrix to include two additional RON = 98, $S \approx 10.5$ fuels, one with a high-olefin content and one with high-cycloalkane content. Acquisition of these additional fuels will be finalized in FY 2017. The compounds used for the four RON = 98, $S \approx 10.5$ fuels were chosen because they represent the various classes of molecules known to provide high sensitivity that are readily available to fuel blenders.

The performance of these fuels is being evaluated in the Sandia LTGC Engine Laboratory using the all-metal single-cylinder LTGC research engine, fitted with a 14:1 compression ratio piston. To provide a performance baseline for these high RON fuels, similar tests were also conducted for a research-quality, Reg-E10 gasoline. For tests to determine the autoignition characteristics of these fuels, the engine is operated in a well-premixed HCCI mode across a wide range of conditions that includes intake pressures (P_{in}) from 1.0 bar to 2.4 bar absolute. Additionally, to determine the potential of using gasoline-like fuels, such as those in the fuels matrix, as fuels for LTGC and other ACI engines, data are also being acquired to measure key parameters for LTGC operation such as the sensitivity of autoignition to variations in the local fuel-air equivalence ratio within the cylinder (ϕ -sensitivity) and the high-load limits attainable over the boost range (1 bar to 2.4 bar). This results in a fairly large engine-operation test matrix for each fuel. Data have been acquired for the Reg-E10 base fuel and for the high-aromatic RON 98 fuel. Performance tests for the other fuels in the matrix will continue in FY 2017.

Results

Autoignition characteristics of these fuels were first evaluated at naturally aspirated conditions ($P_{in} = 1$ bar)

for well-premixed operation in the LTGC engine. Figure 1 shows plots of the combustion phasing (CA50) as a function of intake temperature (T_{in}) for the RON 98 high-aromatic fuel compared to Reg-E10 and a Tier 2 certification fuel with zero ethanol (CF-E0) for the current engine configuration (solid lines). To provide a comparison with a wider variety of fuels, data are also presented for three other fuels acquired with a previous engine configuration that had slightly more restrictive intake ports which produced more charge heating during the intake process (dashed lines). A detailed analysis showed that this additional intake heating was equivalent to raising T_{in} by 2.85°C with the current engine configuration, and accordingly, the T_{in} values plotted in Figure 1 for these three fuels have been increased by this amount for a more correct comparison. Table 1 gives the

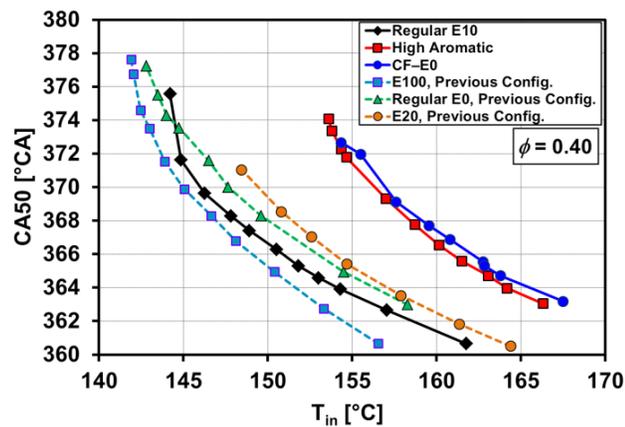


Figure 1. Combustion phasing (CA50) as a function of T_{in} for compression ignition of the various fuels tested. 0° crank angle (CA) is at top dead center (TDC) intake. The fuel-air equivalence ratio (ϕ) = 0.4 for all data points. P_{in} = 1 bar, 1,200 rpm.

octane numbers for all the fuels which include the three fuels discussed above (high-aromatic, Reg-E10, and CF-E0) and the three fuels tested in the previous engine configuration: a zero-ethanol, regular grade gasoline (Reg-E0), this Reg-E0 gasoline blended with 20% ethanol by volume (E20), and neat ethanol (E100).

Examining the figure shows that the high-aromatic fuel and CF-E0, which have relatively high RONs and MONs, require the highest T_{in} for autoignition, indicating that they are the most resistant to autoignition, while Reg-E10 requires a much lower T_{in} in agreement with its lower octane ratings. However, when the other three fuels are considered, the correlation of the relative T_{in} s with RON or MON completely breaks down. Note that E100 has both the highest RON and highest MON, yet it requires the lowest T_{in} at this operating condition.

In an attempt to explain this type of behavior, Kalghatgi and co-workers introduced the Octane Index (OI), defined as $OI = RON - K \cdot S$, where S is defined above in the Approach section, and K varies with engine operating conditions and is determined empirically [2]. Figure 2 shows the CA50 for $T_{in} = 154^\circ\text{C}$ as a function of an OI computed by adjusting K to obtain the best fit to the data in Figure 1. As can be seen, CA50 has a roughly linear relationship to OI, but there is significant scatter in the data. In fact, the high-aromatic fuel and E20 have very nearly the same RON and MON, yet their CA50s vary by more than 7° CA at this T_{in} . These results strongly indicate that using only RON and MON to predict autoignition is not sufficient for LTGC operation, even if the OI is used to extrapolate the data beyond the RON and MON test conditions and it may not be sufficient for advanced SI engines either. In other words, differences in fuel composition can affect autoignition at real-engine conditions in ways that are not accounted for by the RON

Table 1. Fuel Octane Ratings and CA50 and OI Values for $T_{in} = 154^\circ\text{C}$, $P_{in} = 1.0$ bar.

Fuel	CA50	RON	MON	Sensitivity (S)	Octane Index (OI)
Reg-E10	364.1	92.1	84.8	7.3	79.6
High Aromatic	373.0	98.1	87.8	10.3	80.5
CF-E0	372.9	96.0	88.3	7.7	82.9
E100	362.3	109.0	90.0	19.0	76.6
Reg-E0	365.3	91.0	82.7	8.3	76.8
E20	365.9	98.0	87.5	10.5	80.1

and MON tests. It appears that an additional autoignition metric will be required to capture these differences.

Another critical factor for fuel performance in boosted engines is the degree to which autoignition reactions are enhanced by the increased P_{in} . This effect is shown in Figure 3 for the high-aromatic fuel and three other fuels, Reg-E0, E100, and neat cyclopentanone (CPN), a potential biofuel. For each fuel, the figure shows the changes in the bottom dead center temperature (T_{BDC}) required to obtain autoignition with a 10% burn point timing ($CA_{10} \approx 368.7^\circ CA$ or $371.5^\circ CA$ (as noted on the plot) as the P_{in} is increased above naturally aspirated conditions ($P_{in} = 100$ kPa). To make differences in the trends of the various fuels more clear, the T_{BDC} s have been normalized by their values at $P_{in} = 100$ kPa. It can be seen that autoignition reactivity increases with increased P_{in} for all the fuels, as indicated by the decrease in the required T_{BDC} below its value for $P_{in} = 100$ kPa. However, there are large differences between fuels in the amount of T_{BDC} reduction for a given P_{in} increase. Reg-E0 shows the greatest autoignition enhancement with boost, and thus, would be expected to be the most prone to engine knock if it were used in a boosted SI engine. The high-aromatic fuel shows a significantly lower rate of T_{BDC} decrease with boost than Reg-E0, and it does not reach a T_{in} of $60^\circ C$ (the lowest T_{in} used for fully premixed fueling) until $P_{in} = 220$ kPa, compared to only 180 kPa for Reg-E0. This is in agreement with the higher RON and S of the high-aromatic fuel. However, E100 shows almost the same T_{BDC} reduction with boost as the high aromatic fuel, despite its significantly higher RON, MON, and S, indicating that RON and MON are most likely not sufficient autoignition and knock metrics for boosted operation. Finally, CPN shows the least reduction in T_{BDC}

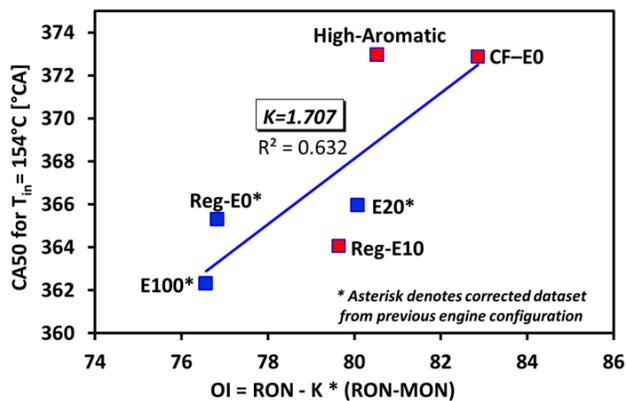


Figure 2. The best fit of OI to the CA50 values from Figure 1 for $T_{in} = 154^\circ C$. As noted in the plot, the best fit was for $K = 1.707$ but this gives a low $R^2 = 0.632$ in agreement with the scatter in the data.

with boost suggesting that it might be a very good fuel for preventing knock in high-boost engines.

As mentioned in the Approach section, ϕ -sensitivity is an important fuel characteristic for LTGC and some other ACI engines. To determine the potential of the gasoline-like, high-aromatic fuel for use in these engines, ϕ -sensitivity tests were conducted for this fuel and for Reg-E10. For these tests, the LTGC engine was first operated with fully premixed fueling for a range of equivalence ratios, and for each data point, CA50 was advanced until the ringing intensity (RI) = $5 MW/m^2$ which gives the most advanced CA50 without knock. RI is a measure of the engine's propensity to knock [3], and $RI = 5 MW/m^2$ has been shown to be the highest RI without knock in our LTGC engine [4]. Then the charge mixture was partially stratified using a fueling technique called standard partial fuel stratification (std-PFS), in which 90% of the fuel is premixed and 10% is directly injected at $310^\circ CA$ (50° before TDC compression). This produces a distribution of ϕ s in the cylinder, and if the fuel is ϕ -sensitive, the various ϕ s autoignite sequentially from richest to leanest, reducing the heat release rate (HRR). The lower HRR reduces the RI, allowing CA50 to be further advanced before reaching the $RI = 5 MW/m^2$ limit [5,6]. The more ϕ -sensitive the fuel, the greater the reduction in HRR with std-PFS and the greater the CA50 advancement compared to fully premixed fueling. Figure 4 shows the results of these tests for a range of P_{in} s for both the

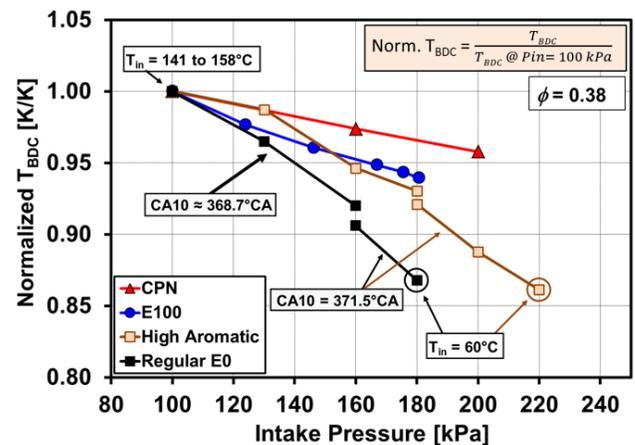


Figure 3. Comparison of the autoignition reactivity enhancement with boost for various fuels. The reduction in normalized T_{BDC} with increased P_{in} provides a measure of the autoignition reactivity enhancement. As shown at the upper right of the plot, T_{BDC} has been normalized by its value at $P_{in} = 100$ kPa (units = K/K). $\phi = 0.38$, 1,200 rpm. CA10 is held constant at two different values as shown in the plot. $0^\circ CA$ is at TDC intake.

Reg-E10 and high-aromatic fuels. The difference in CA50 between the premixed (solid lines) and std-PFS (dashed lines) shows that Reg-E10 is strongly ϕ -sensitive from $P_{in} = 2.4$ bar to 1.6 bar and still moderately ϕ -sensitive at $P_{in} = 1.3$ bar. In contrast, the high-aromatic fuel is only strongly ϕ -sensitive at $P_{in} \geq 2.0$ bar (only 2.0 bar is shown), moderately ϕ -sensitive at 1.6 bar, and it shows no ϕ -sensitivity for $P_{in} = 1.3$ bar or lower. The high-aromatic fuel's low ϕ -sensitivity at lower P_{in} s will limit its potential as a fuel for LTGC and some other ACI concepts.

Because previous works have shown a strong correlation between ϕ -sensitivity and the amount of intermediate temperature heat release (ITHR) [7], the ITHR was examined for the Reg-E10 and high-aromatic fuels for P_{in} s from 1.0 bar to 2.4 bar as shown in Figure 5. These curves show the very early part of the HRR, prior to hot autoignition, on an amplified scale. In this plot, the CA10s have been precisely aligned so the differences in the early HRR are more clear. With this offset, all the curves converge by about -3° , at which point the HRR is rising rapidly indicating the onset of hot ignition. The ITHR is the heat release occurring from about -17° until this

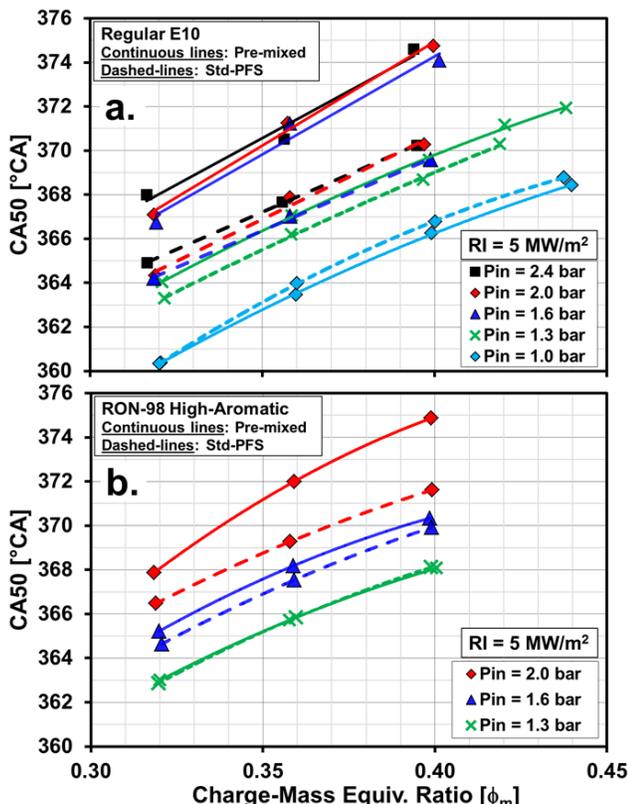
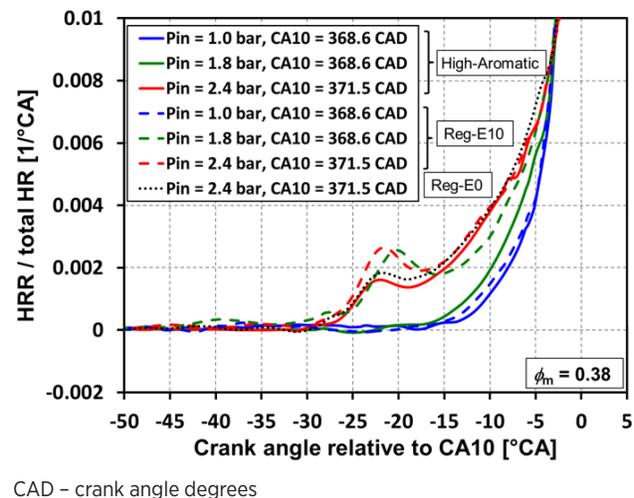


Figure 4. ϕ -sensitivity as shown by the difference in CA50 between pre-mixed (solid lines) and std-PFS fueling (dashed lines) for the Reg-E10 (a) and the high-aromatic (b) fuels. RI = 5 MW/m^2 for all points, 1,200 rpm. 0° CA is at TDC intake.

rapid rise at -3° . Some higher P_{in} curves show a distinct low-temperature heat release (LTHR) bump from about -29° to about -17° , and the ITHR is considered to begin at the local minimum after the LTHR at about -17° . For other conditions, there is no detectable LTHR and the first detectable heat release occurs from ITHR reactions at about -17° . As the figure shows, both fuels have relatively low values of ITHR at $P_{in} = 1$ bar and high values for $P_{in} = 2.4$ bar. However, at an intermediate $P_{in} = 1.8$ bar for the high-aromatic fuel, the ITHR is only slightly above the $P_{in} = 1$ bar curves, whereas, for the Reg-E10 it is nearly the same as for $P_{in} = 2.4$ bar. These ITHR trends are in very good agreement with the differences in ϕ -sensitivity shown by the data in Figure 4, confirming that the correlation between ITHR and ϕ -sensitivity also holds for this high-RON, high-S, fuel. These detailed analyses of LTHR and ITHR are also valuable for chemical-kinetic model development and validation.

Conclusions

- A test matrix for gasoline-like fuels has been established in collaboration with ORNL to provide an understanding of the fuel properties required to predict anti-knock and autoignition characteristics in advanced, boosted engines, both SI and ACI.
- The initial matrix consists of three RON 98 fuels, one with low-S, and two with high-S, but different compositions (high-aromatic and high-ethanol fuels).



CAD – crank angle degrees

Figure 5. Comparison of changes in ITHR with P_{in} for the High-Aromatic and Reg-E10 fuels. Additionally, Reg-E0 at $P_{in} = 2.4$ bar is shown for comparison. The HRR has been normalized by the total HRR for each condition to remove differences caused only by changes in the total fueling as P_{in} is varied.

- An effort is underway to expand this fuel matrix to include RON 98, high-S fuels with high-olefin and high-cycloalkane content.
- For well-mixed naturally aspirated LTGC, the high-aromatic fuel requires a much higher T_{in} to reach autoignition at a given CA50 than the Reg-E10 gasoline tested in this study, in agreement with its higher RON and MON.
 - However, comparison of these data with data from four other fuels tested in previous studies shows no overall correlation between the required T_{in} and RON, MON, or S.
- Applying the OI [2] to the high-aromatic, Reg-E10 and other four fuels showed that it provided only a weak correlation, indicating that an additional autoignition metric may be required.
- The high-aromatic fuel showed a significantly lower rate of autoignition enhancement with increasing intake boost than Reg-E0, indicating it has good anti-knock potential for boosted SI engines.
- The high-aromatic fuel required significantly more intake boost to become ϕ -sensitive than Reg-E10, indicating that it has limited potential for LTGC and some other ACI concepts.
 - Changes in the amount of ITHR showed a strong correlation with ϕ -sensitivity as found in other studies suggesting that measuring the ITHR may be a method for the rapid screening of fuels for ϕ -sensitivity.

References

1. Yang, Y., Dec, J.E., Sjöberg, M., and Ji, C., "Understanding Fuel Anti-Knock Performances in Modern SI Engines Using Fundamental HCCI Experiments," *Combustion and Flame*, **162**, pp. 4006–4013, 2015.
2. Risberg, P., Kalghatgi, G. and Ångström, H.-E., "Autoignition Quality of Gasoline-Like Fuels in HCCI Engines," SAE Technical Paper 2003-01-3215, 2003, doi:10.4271/2003-01-3215.
3. Eng, J.A., "Characterization of Pressure Waves in HCCI Combustion," SAE Technical Paper 2002-01-2859, 2002, doi:10.4271/2002-01-2859.
4. Dernotte, J., Dec, J.E., and Ji, C., "Energy Distribution Analysis in Boosted HCCI-like / LTGC Engines – Understanding the Trade-offs to Maximize the Thermal Efficiency," SAE Technical Paper 2015-01-0824 and *SAE Int. J. Engines* 8(3): 956–980, 2015, doi:10.4271/2015-01-0824.
5. Dec, J.E., Yang, Y., and Dronniou, N., "Boosted HCCI – Controlling Pressure-Rise Rates for Performance Improvements using Partial Fuel Stratification with Conventional Gasoline," *SAE Int. J. Engines*, **4**(1): 1169–1189, 2011, doi:10.4271/2011-01-0897.
6. Dec, J.E., Yang, Y., and Dronniou, N., "Improving Efficiency and using E10 for Higher Loads in Boosted HCCI Engines," SAE Technical Paper 2012-01-1107, *SAE Int. J. Engines* 5(3):1009–1032, 2012, doi:10.4271/2012-01-1107.
7. Yang, Y., Dec, J.E., Dronniou, N. and Cannella, W., "Boosted HCCI Combustion Using Low-Octane Gasoline with Fully Premixed and Partially Stratified Charges," *SAE Int. J. Engines* 5(3): 1075–1088, 2012, doi:10.4271/2012-01-1120.

FY 2016 Publications/Presentations

1. Miles, P.C. et al. Advanced Engine Development Team Report for the DOE Annual Merit Review, Office of Vehicle Technologies, June 2016.
2. Dernotte, J., Dec, J.E., and Ji, C., "Evaluation of LTGC Engine Performance with a Low-Swirl Cylinder Head and the Potential of PFS for Timing Control," DOE Advanced Engine Combustion Working Group Meeting, February 2016.
3. Dec, J.E., Dernotte, J. and Ji, C., "Fuel Effects on LTGC Combustion – Initial Results with a Co-Optima Fuel," presented to General Motors Research staff, August 2016.
4. Dernotte, J., Dec, J.E., Ji, C. and Gentz, G., "Determining Octane Index (OI) and K for Naturally Aspirated LTGC," presented to General Motors Research staff, October 2016.

Special Recognitions & Awards/ Patents Issued

1. U.S. Patent Application Filed, No. 14/855,809: Dec, J.E. and Renzi, R., September 2015.
2. DOE EERE Special Recognition Award – For research on diesel engine and HCCI-like combustion. Presented by DOE at the Annual Merit Review, June 2016.
3. USCAR Team Award for work on the U.S. DRIVE ACEC Fuels Roadmap Sub-Team.

III.3 Accelerate Development of ACI/LTC: ORNL Single- and Dual-Fuel ACI

Overall Objectives

- The overall objective of the Co-Optimization of Fuels & Engines Initiative (Co-Optima) is to cooperatively develop emerging biofuels and advanced engines to bring these technologies to the market sooner to realize a reduction in petroleum consumption.
- This project aims to investigate the validity of the Co-Optima central fuel hypothesis, which states that fuels that a fuel candidate should perform in a manner commensurate with its properties regardless of its chemistry.
- Specifically, this project is investigating the potential of the co-evolution of fuels and a subset of combustion strategies: single- and dual-fuel advanced compression ignition (ACI).

Fiscal Year (FY) 2016 Objectives

- To gain a greater understanding of the fuel effects for high and low reactivity fuels on single-fuel and dual-fuel ACI concepts to realize the goals of taking advantage of fuel properties for attaining higher efficiency in ACI engines through metal engine experiments and collaboration with optical experiments performed at Sandia National Laboratories (SNL)
- Identify performance trends in ACI strategies spanning broad landscape of ACI modes with the targeted fuel properties identified
- Quantify the increase in the dual-fuel reactivity controlled ACI operating range due to the use of renewable fuels with transient hardware-in-the-loop experiments

FY 2016 Accomplishments

- Demonstrated transient ACI via hardware-in-the-loop experiments and boosted, spark-ignition (SI) fuels
- Collaboration with SNL linking optical and metal experimental ACI results established
- Published gasoline compression ignition (GCI) perspective paper linking ACI modes across of spectrum of stratification

Scott Curran (Primary Contact), Martin Wissink, Robert Wagner

Oak Ridge National Laboratory (ORNL)
2360 Cherahala Blvd.
Knoxville, TN 37932
Phone: (865) 946-1522
Email: curransj@ornl.gov

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
University of Wisconsin-Madison, Madison, WI

Future Directions

- Complete coordinated experiments with SNL with selected fuel combinations for high- and low-delta dual-fuel ACI modes
- Complete experimental campaign and data processing to assess fuel effects on emissions and efficiency for ACI combustion modes in support of merit function development
- Investigate potential of ACI modes with electrified powertrains
- Transient experiments for research into fuel effects on ACI modes ■

Introduction

Previous research into the role that fuel properties can have on expanding ACI operating load and increasing efficiency have netted valuable results. Previous ORNL fuel effects research has focused on ACI load expansion in terms of drive cycle coverage with the goal of increasing potential fuel economy benefits. By covering more of the U.S. light-duty drive cycle range, the potential for increasing fuel economy benefits over conventional combustion baselines had been shown to be higher. The Co-Optima initiative is looking at extending the current understanding of fuel effects on ACI performance and co-optimizing engines and fuels for higher potential fuel savings and greenhouse reductions. By using the Co-Optima approach to understand the roles that critical fuel

properties have broadly on ACI engine performance, a basis for co-optimization can be established. Fuel effects are being investigated in the support of developing an ACI Merit Function 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.

Approach

Advanced engine experiments in support of the DOE Co-Optima goals focusing on ACI approaches were performed in a light-duty multi-cylinder engine laboratory. The research platform is a 4-cylinder General Motors 1.9-L direct injection turbocharged diesel engine modified to include a port fuel injection system using conventional gasoline injectors and a direct injection fuel system capable of running diesel-range and gasoline-range fuels. A flexible microprocessor-based control system allowed for control over both fueling systems and complete authority over engine operating parameters allowing operation of both single-fuel and dual-fuel advanced combustion modes. In addition, the ORNL advanced combustion engine laboratory has been integrated with a hardware-in-loop setup allowing full drive cycle with the hardware-in-loop system simulating the rest of the vehicle and controlling the driver behavior

including shifting. A schematic of the transient enabled advanced combustion platform capable of dual-fuel or single-fuel ACI modes is shown in Figure 1.

In addition to the multi-cylinder metal ACI engine experiments, ORNL is collaborating with a team from SNL to gain deeper insight into fuel specific effects around ACI modes. This collaboration is focused on matching metal engine experiments to the optical work at SNL initially with matched primary reference fuel (PRF) mixtures. Further collaborations will focus on isolating the physical and chemical fuel effects on ACI development including joint research projects with researcher exchange planned for FY 2017.

Results

A review paper focusing on GCI and understanding the landscape of a wide range of advanced combustion modes and importance of fuel effects in these modes was completed and published online first in the *International Journal of Engine Research* [1]. The article provides an overview and perspective of the current research efforts to develop engine operating strategies for achieving gasoline low temperature combustion (LTC) in a compression ignition engine via fuel stratification. In this study, computational fluid dynamics modeling of the in-cylinder processes during the closed valve portion of the cycle was used to illustrate the opportunities and challenges

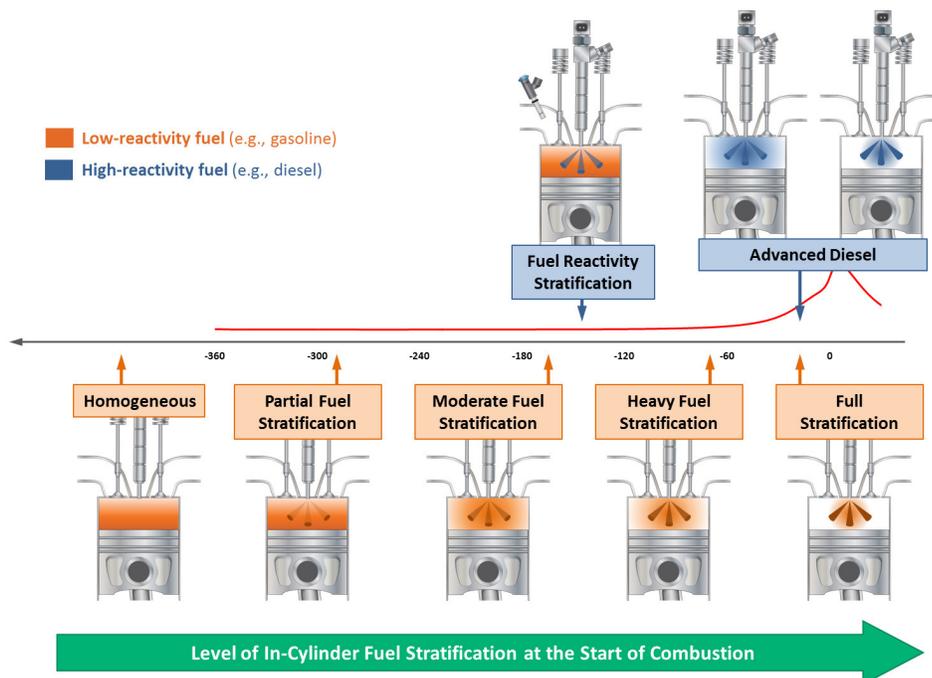
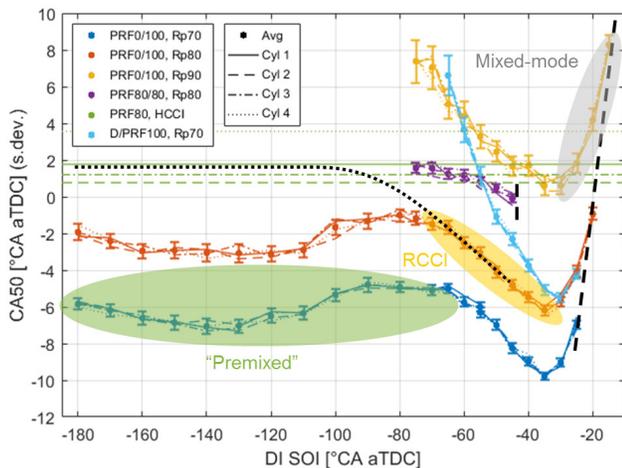


Figure 1. Landscape of ACI combustion strategies aimed at achieving high-efficiency and low emissions

associated with the various fuel stratification levels. This perspective of investigating LTC on a continuum of in-cylinder stratification as shown in Figure 1 is critical to informing new research efforts focused on achieving potential efficiency gains and emissions reductions with these related LTC modes.

A collaborative experimental effort was initiated examining the fuel effects with reactivity controlled compression ignition (RCCI) between the multi-cylinder metal advanced combustion engine (MCE) at ORNL and Mark Musculus at SNL using his lab’s optical engine. The purpose of the collaborations is to better understand the ability for a single fuel to be split apart and used for dual-fuel. Experimental results will help answer questions related to discerning fuel effects from reactivity stratification effects for co-optimization of ACI modes with proposed fuels. Regular telecons are underway between the SNL and ORNL teams. Coordination on initial PRFs for initial experiments will allow closer comparison between optical results and MCE results used that will allow for optical diagnostics underway.

MCE experiments using PRF0 (n-heptane) and PRF100 (iso-octane) across a wide range of main start of injection (SOI) timings and different premixed ratios have been completed as shown in Figure 2. The fuel choices and operating conditions were chosen to allow for best matching during the collaborations with SNL on matched optical experiments to be able to decouple physical and chemical effects. The addition of fuel reactivity as a variable significantly expands the operating envelope.



°CA – degrees crank angle; aTDC – after top dead center; CA50 – crank angle for 50% burn

Figure 2. RCCI controllability with various premixed ratios (rP = 70%, 80% and 90% PRF100) over wide main direct injection timing sweep

Results in Figure 3 show the relative impact of fuel reactivity gradients vs. equivalence ratio gradients and their utility for control authority over the combustion process.

Results of the GCI fuel effects experiments using the gasoline-range fuels supplied by Chevron Energy Technologies in partial fuel stratification and heavy fuel stratification (HFS) modes were completed and the analysis of the results is ongoing in addition to the Co-Optima focused research in support of knowledge discovery around the topic. Results of a comparison of emissions performance of HFS with a PRF blend and a 70 Research Octane Number (RON) is shown in Figure 4. These results are part of the larger GCI/RCCI comparison in collaboration with Chevron who is supplying the gasoline-range fuels of interest for GCI operation. The experiments investigated the role of RON ranging from <40 to 87 both for partial fuel stratification and HFS low temperature GCI modes.

Conclusions

- Metal engine results have identified key regions of interest and establishes a baseline for continuing collaboration between ORNL and SNL via metal and optical engine experiments.
- Initial collaboration results have set the stage for probing the intersection and relative importance of both the physical and chemical properties of fuels as they pertain to RCCI operation. Improving the understanding of these factors will be vital to the development of an ACI merit function.

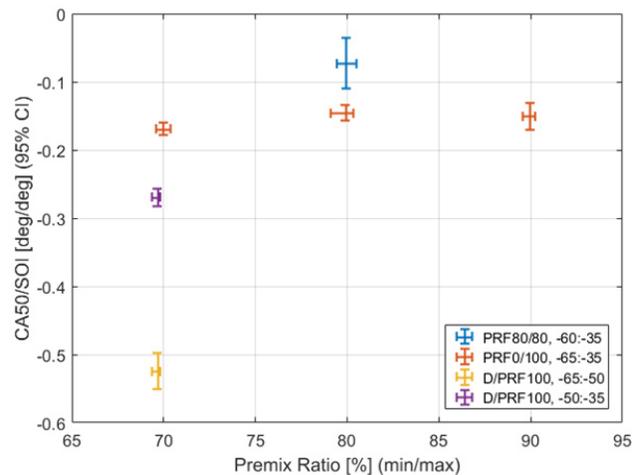
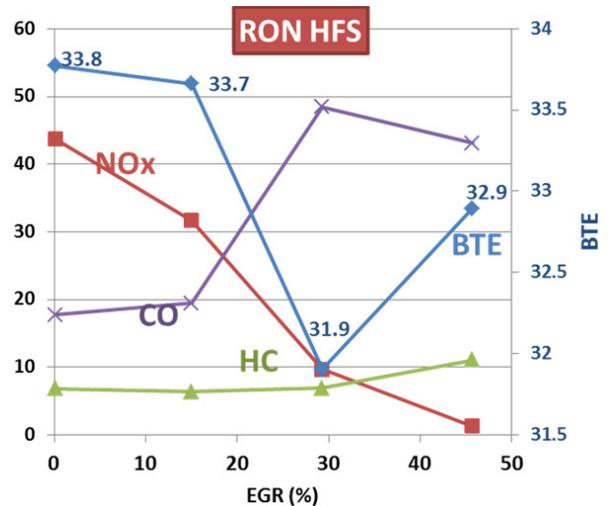
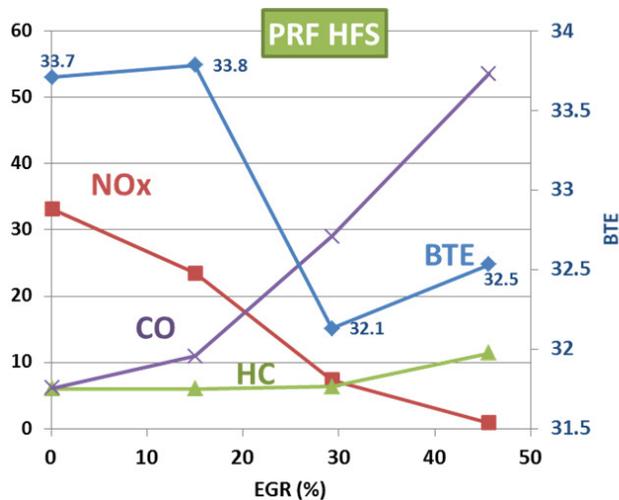


Figure 3. Combustion phasing (CA50) authority as a function of SOI for the different fuel combinations



BTE - brake thermal efficiency; HC - hydrocarbon

Figure 4. Exhaust gas recirculation (EGR) sweep with HFS. Note higher NO_x emissions with 70 RON gasoline at 0% EGR due to higher maximum pressure rise rate/earlier main SOI for maintaining combustion phasing of 8°CA atDC.

- New perspective defines a combustion mode continuum that unites how all of these previously thought “individual” combustion modes relate to one another through the degree of air/fuel stratification at the time of combustion. With the realization that these modes are related, researchers may have more flexibility in exploring the role of fuel effects on expanding ACI to cover engine operating load range and help avoid problems related to emissions controls.
- The use of the combination of metal engine and optical engine experiments to explore the role of physical and chemical differences in Co-Optima fuels of interest is expected to provide new insights in co-optimization of ACI engines and fuels.
- The capability to investigate transient fuel effects on ACI modes has been demonstrated and is expected to provide new and valuable research results in the future.

References

1. Dempsey, A.B, Curran, S.J., and Wagner, R.M., A perspective on the range of gasoline compression ignition combustion strategies for high engine efficiency and low NO_x and soot emissions: Effects of in-cylinder fuel stratification,” 2016, *International Journal of Engine Research*, DOI: 10.1177/1468087415621805.

FY 2016 Publications/Presentations

1. Wagner, R., “Directions in High Efficiency Engine Research and Future Fuel Opportunities,” Missouri

University of Science and Technology, Rolla, MO, September 2016.

2. Curran, S.J, “Fuel Effects on Accelerating Advanced Compression Ignition,” Presentation to Co-Optima LGGF Team, August 2016.
3. Curran, S.J, “Fuel Effects Accelerating Advanced Compression Ignition Concepts,” Presentation to DOE FLT program manager, July 2016.
4. Dempsey, A.B, Curran, S.J., and Wagner, R.M., A perspective on the range of gasoline compression ignition combustion strategies for high engine efficiency and low NO_x and soot emissions: Effects of in-cylinder fuel stratification,” 2016, *International Journal of Engine Research*, DOI: 10.1177/1468087415621805.
5. Curran, S., Wagner, R., “Reactivity Stratified Combustion Development for Light-Duty Multi-Cylinder Engines,” IEA Technology Collaboration Programmes (TCP) for Clean and Efficient Combustion, 38th Task Leaders Meeting in Ruka, Finland, June 26 to June 30, 2016.
6. Curran, S., “Well-to-wheel comparison of multi-mode advanced combustion strategies and other advanced light duty vehicle technologies,” 2016 SAE World Congress, April 2016, Detroit, MI, USA.
7. Curran, S., “Update on Single-/Dual-Fuel Low Temperature Combustion Light-Duty Multi-Cylinder Research at ORNL,” AEC Program Review, Livermore, CA, February 2016.

8. Wagner, R.M., "Engines of The Future," *Mechanical Engineering: The Magazine of ASME*, No 12. 137, December 2015.

Special Recognitions and Awards/ Patents Issued

1. Green Car Congress review of GCI review article,
<http://www.greencarcongress.com/2016/01/20160118-orl.html>

III.4 Accelerate Development of ACI/LTC: Fuel Effects on RCCI Combustion

Overall Objectives

- Measure in-cylinder mixing and kinetics to optimize dual-fuel heat release for noise, efficiency, and load range
- Understand mixing–ignition interaction for different fuel reactivity combinations
- Support metal engine reactivity controlled compression ignition (RCCI) E.2.2 task work at Oak Ridge National Laboratory (ORNL)

Fiscal Year (FY) 2016 Objectives

- Verify that operating condition trends and characteristics observed in RCCI experiments in light-duty multi-cylinder all-metal engine at ORNL can be reproduced in the heavy-duty single-cylinder optical engine at SNL
- Use high-speed visible combustion luminosity imaging to identify how in-cylinder processes affect engine performance as operating conditions change
- Use infrared (IR) emission diagnostics to measure fuel–jet penetration and to characterize in-cylinder fuel mixture distributions

FY 2016 Accomplishments

- Characteristic features and trends in the apparent heat release rate (AHRR) for injection timing sweeps in the optical engine mirror those observed for the metal engine. Although key AHRR features occur at different timings in the two facilities, the characteristic behavior is the same, such that comparisons of data from the two experiments at operating conditions with similar AHRR features can provide insight into how in-cylinder processes observed in the optical engine affect engine performance and emissions observed in the all-metal engine.
- Imaging data confirm expectations based on ignition delay trends that premixing controls the peak AHRR, and hence play a role in the load limits of RCCI. IR emission imaging also reveals that inhomogeneities in the more well-mixed gasoline direct injection (GDI) charge may also play a role in the AHRR characteristics.

Mark P.B. Musculus

Sandia National Laboratories (SNL)

PO Box 969, MS 9053

Livermore, CA 94551-0969

Phone: (925) 294.3435

Email: mpmuscu@sandia.gov

DOE Technology Development Manager:

Kevin Stork

Future Directions

- Build on knowledge gained from FY 2016 experiments at ORNL and SNL, develop a joint experimental design to provide the most meaningful comparisons of data acquired from the two engine facilities
- Apply quantitative mixing diagnostics to understand how engine hardware and operating conditions can be designed to help overcome operating condition range limits of RCCI for baseline test fuels
- Apply optical diagnostics using fuels with varying properties to understand how fuel properties couple with engine hardware and operating conditions at the operating condition range limits of RCCI ■

Introduction

Many advanced combustion approaches have demonstrated the potential for achieving diesel-like thermal efficiency but with much lower pollutant emissions of particulate matter and nitrogen oxides. RCCI is one advanced combustion concept, which makes use of in-cylinder blending of two fuels with differing reactivity for improved control of the combustion phasing and rate [1]. Previous research and development at ORNL has demonstrated successful implementation of RCCI on a light-duty multi-cylinder engine over a wide range of operating conditions [2]. Several challenges were encountered when extending the research to practical applications, including limits to the operating range, both for high and low loads.

Co-optimizing the engine and fuel aspects of the RCCI approach might allow these operating limits to be overcome. The in-cylinder mechanisms by which fuel

properties interact with engine operating condition variables is not well understood, however, in part because RCCI is a new combustion concept that is still being developed, and limited data have been acquired to date, especially using in-cylinder optical and imaging diagnostics. The objective of this work is to use in-cylinder diagnostics in a heavy-duty single-cylinder optical engine at SNL to understand the interplay between fuel properties and engine hardware and operating conditions for RCCI in general, and in particular for the light-duty multi-cylinder all-metal RCCI engine experiments at ORNL.

Approach

This project uses an optically accessible, heavy-duty, direct injection diesel engine (Figure 1). To achieve dual-fueling for RCCI, a Bosch gasoline direct injector operating with iso-octane at a fuel pressure of 100 bar was added in place of one of the five cylinder wall windows (see Figure 1). For diesel-type fuels, the engine retains a centrally located heavy-duty common rail (CR) injector operating with n-dodecane at a rail pressure of 500 bar. A large window in the piston crown provides primary imaging access to the piston bowl, and other windows at

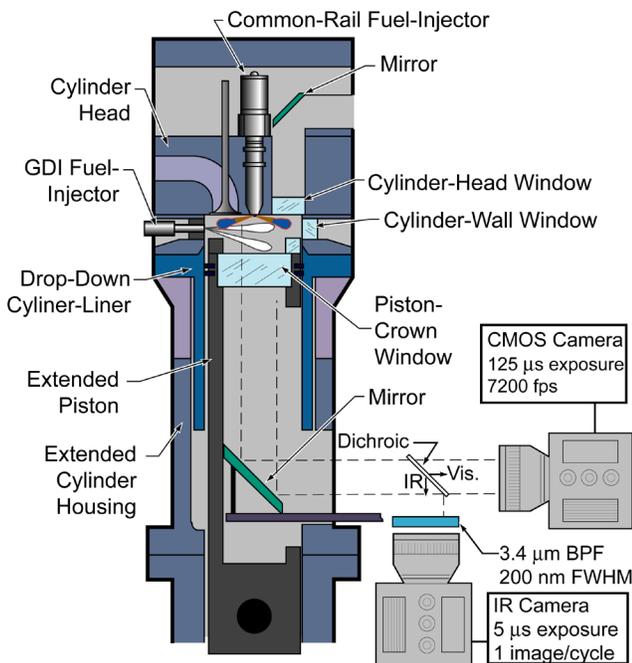
the cylinder wall provide cross-optical access for laser diagnostics or imaging.

The optical engine experiment shown in Figure 1 uses two cameras for simultaneous imaging of in-cylinder IR and visible light emissions. The beamsplitter reflects IR emission to an IR camera that records one image per cycle at an exposure of $5 \mu\text{s}$. The camera is equipped with a bandpass filter centered at $3.4 \mu\text{m}$ with a passband of 200 nm, which was chosen to isolate emission from hot fuel vapors. After ignition, the camera also records emission from other combustion-generated sources. The visible light emission passes through the beamsplitter and is directed to a high-speed CMOS camera with an exposure of $125 \mu\text{s}$ and a frame rate of 7,200 fps (one image per crank angle degree).

Results

Figure 2 shows AHRR data for a timing sweep of the CR injection of the high-reactivity n-dodecane fuel from a start of injection (SOI) of -50 crank angle degrees (CAD) after top dead center (ATDC) to -10 CAD ATDC while holding the gasoline direct injector injection timing of the low-reactivity iso-octane fuel constant at -270 CAD ATDC. To avoid clutter in the plots, the AHRR data are divided into two plots, with the top plot showing the first half of the sweep from -50 to -30 CAD ATDC, and the bottom plot showing the second half from -30 to -10 CAD ATDC, as indicated by the legend and annotations on the figure. The nominal load is 5 bar gross indicated mean-effective pressure (GIMEP) and 80% of the fuel energy is delivered by the GDI injection of iso-octane, with the balance delivered by the CR injection of n-dodecane.

The AHRR trends show a characteristic progression of advancing combustion phasing with increasing peak AHRR during the first half of the sweep (Figure 2, top), followed by a reversal with retarding combustion phasing and decreasing peak AHRR over the second half of the sweep. Throughout the sweep, the ignition delay for the CR fuel is monotonically decreasing, indicating less time for premixing. Hence, as the degree of premixing of the CR fuel decreases, the peak AHRR at first increases and then decreases. At the intermediate CR injection timing, where the peak AHRR is highest, achievable engine load becomes limited by excessive noise and pressure rise rates as the injection durations are increased to provide higher fuel delivery. Similar trends are observed in the metal engine tests at ORNL, though with different CR SOI values for the key features of the AHRR characteristics. Hence, although differences in the engine hardware between the light-duty multi-cylinder all-metal engine and the heavy-duty single-cylinder



CMOS – complementary metal-oxide semiconductor; FWHM – full width at half maximum; BPF – Berkeley Packet Filter; Vis. – visible

Figure 1. Schematic diagram of the heavy-duty single-cylinder optical diesel engine and optical setup with IR emission and visible natural combustion luminosity cameras

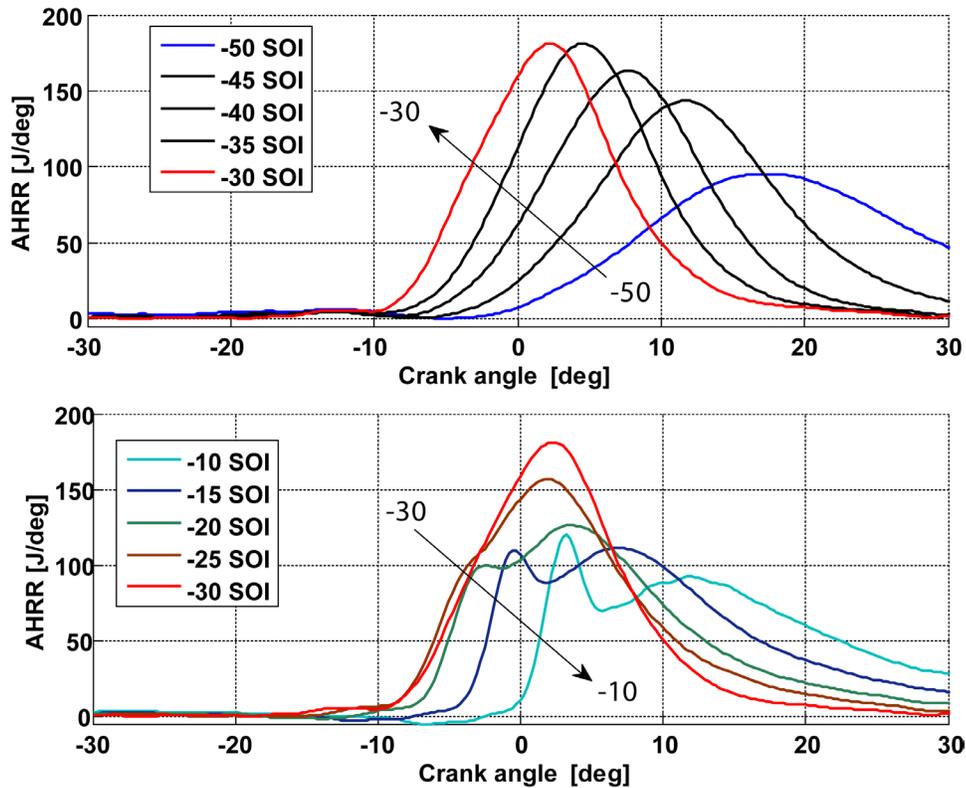


Figure 2. AHRR for a timing sweep of the CR injection (n-dodecane) SOI = -50 to -30 CAD ATDC (top) and from -30 to -10 CAD ATDC (bottom) at a constant gasoline direct injector (iso-octane) timing of -270 CAD ATDC. 5 bar GIMEP, 80% iso-octane.

optical engine alter the CR SOI timing where key AHRR features are manifest, the same characteristic trends are common between the engines, such that comparisons of data from the two experiments at operating conditions with similar AHRR features can provide insight into how in-cylinder processes observed in the optical engine may affect engine performance and emissions observed in the all-metal engine.

For example, Figure 3 shows typical images of natural combustion luminosity at the peak AHRR (left) and IR emission at the start of combustion (SOC, right) at three selected CR SOI timings from Figure 2. The field of view for the visible luminosity images covers the entire piston bowl, while the IR camera field of view spans a rectangular portion of the bowl indicated by the dashed rectangles overlaid on the visible images.

For the earliest CR SOI timing of -45 CAD ATDC (top row), the visible emission at the peak AHRR (left) is relatively uniform, indicating relatively premixed conditions without any stoichiometric or fuel-rich regions that would produce strong natural luminosity, with the exception of a few bright spots caused by a small amount

of fuel that dribbles from the CR injector after the end of injection (which is typical for CR diesel injectors) [3]. At the CR timing of -35 CAD ATDC (middle row), which has the highest peak AHRR of the CR timing sweep in Figure 2, the natural luminosity image shows large blobs of brighter emission, which is characteristic of locally stoichiometric or potentially fuel-rich mixtures. Retarding the CR SOI timing further to -20 CAD ATDC (bottom row) shows even more broad regions of bright emission, indicating even less premixing, consistent with expectations based on decreasing ignition delay.

The IR images at SOC provide further insight, showing increasing bright emission arising from early combustion reactions (black color) with more distinct residual jet structure as the CR SOI timing is retarded, indicating reduced premixing. Additionally, the IR data provide some indication of some mixture heterogeneity in the underlying GDI iso-octane charge (pink to red color). Regions with weak emission in the IR images (e.g., pink color in the bottom left of the top two IR images) correspond well with regions of low emission in the same areas of the visible combustion luminosity images (left column). Hence, in addition to the role of changes in the

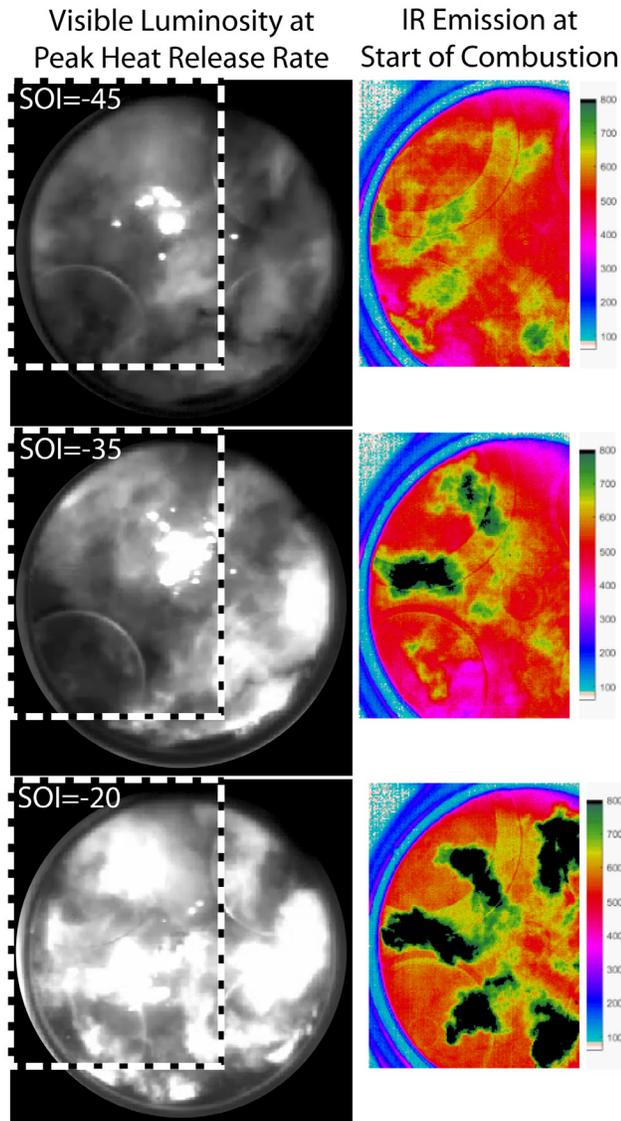


Figure 3. Images of natural combustion luminosity at the peak AHRR (left) and IR emission at SOC (right) at three selected CR SOI timings. The field of view for the visible luminosity images covers the entire piston bowl, while the IR camera field of view spans a portion of the bowl indicated by the dashed rectangles overlaid on the visible images.

amount of CR fuel premixing on the AHRR characteristic features, the IR imaging shows that inhomogeneities in the more well-mixed GDI charge may also play a role, at least for the injection hardware employed in the optical engine.

Future research will use additional laser and optical diagnostics to measure in-cylinder fuel concentration distributions to help to quantify the effects of those mixture distributions on ignition and combustion.

Additionally, fuel properties including volatility and/or reactivity will be varied to better understand the interplay between fuel properties and operating conditions. Together with the all-metal engine experiments at ORNL, these data will help to provide insight into how the load limits of RCCI might be overcome through the Co-Optimization of Fuels & Engines.

Conclusions

- Although differences in the engine hardware between the light-duty multi-cylinder all-metal engine and the heavy-duty single-cylinder optical engine alter the CR SOI timing where key ARHH features are manifest, the same characteristic trends are common between the engines, such that comparisons of data from the two experiments at operating conditions with similar AHRR features can provide insight into how in-cylinder processes observed in the optical engine may affect engine performance and emissions observed in the all-metal engine.
- Retarding the CR SOI timing leads to larger and brighter localized emission in the natural luminosity images at the peak AHRR, as well as more well-defined residual jet structures in the IR images at SOC, indicating decreasing premixing, confirming expectations based on decreasing ignition delay.
- IR imaging also shows that inhomogeneities in the more well-mixed GDI charge may also play a role in the AHRR characteristics, at least for the injection hardware employed in the optical engine.

References

1. R.D. Reitz, G. Duraisamy, "Review of high efficiency and clean reactivity controlled compression ignition (RCCI) combustion in internal combustion engines," *Progress in Energy and Combustion Science* 46:12–71, 2015.
2. S.J. Curran, Z. Gao, V.Y. Prikhodko, A.B. Dempsey, J.M. Storey, J.E. Parks, R.M. Wagner, "High efficiency clean combustion in light-duty multi-cylinder diesel engines," *Advanced Combustion Engines 2015 Annual Report*, DOE Vehicle Technologies Office, 2015.
3. M.P.B. Musculus, "Heavy-duty low-temperature and diesel combustion & heavy-duty combustion modeling," *Advanced Combustion Engines 2014 Annual Report*, DOE Vehicle Technologies Office, 2014.

FY 2016 Publications/Presentations

1. “Optical imaging to understand fuel reactivity effects on RCCI combustion,” W.E. Eagle, G. Roberts, M.P.B. Musculus, presentation at AEC Working Group Meeting, August 2016.
2. “Co-optimization of fuels and engines, advanced engine development team,” P. Miles, M. Sjöberg, J. Dec, S. Ciatti, C. Kolodziej, S. Curran, M. Musculus, C. Mueller, Advanced Combustion Engines 2016 Annual Report, DOE Vehicle Technologies Office, 2016.

III.5 Improved Mixing-Controlled Combustion Technologies and Fuels for High-Efficiency Compression Ignition Engines

Overall Objectives

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

- New technologies to dramatically increase the performance per unit cost of future high-efficiency engine and fuel systems
- High-quality experimental data for computational fluid dynamics model development to facilitate accurate, rapid, and cost-effective computational engine optimization for new technologies
- A fundamental understanding of fuel composition and property effects on mixing-controlled combustion strategies by formulating and studying the performance of chemically and physically well-characterized reference fuels made from blending stocks as well as pure compounds

Fiscal Year (FY) 2016 Objectives

- 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 six-hole injector tip and a commercial #2 ultra-low-sulfur diesel certification fuel (CF) in neat form or blended with an oxygenate
- Determine the extent to which ducted fuel injection (DFI), i.e., directly injecting fuel through a small tube aligned with the fuel spray, can increase the degree of fuel/charge-gas premixing present in the autoignition zone, thereby achieving LLFC without requiring the use of an oxygenated fuel
- Investigate the importance of the liquid phase fuel penetration length and the flame lift-off length (i.e., the axial distances from the injector orifice exit to the most downstream location of liquid fuel droplets and to the autoignition zone, respectively) on soot emissions from mixing-controlled compression ignition (CI) combustion

**Charles J. Mueller (Primary Contact),
Ryan K. Gehmlich,
Christopher W. Nilsen, Daniel J. Ruth,
and Yefu Wang**

Sandia National Laboratories
7011 East Ave., MS 9053
Livermore, CA 94550-9517
Phone: (925) 294-2223
Email: cjmuell@sandia.gov

DOE Technology Development Manager:
Kevin Stork

FY 2016 Accomplishments

- Provided the first conclusive experiments showing that LLFC can be sustained in an engine to ~20% load using a realistic fuel injector configuration (i.e., a six-hole tip), practical operating conditions, and a feasible fuel. Fuel oxygenation was required, and one or more additional mixing enhancement strategies will be necessary to sustain LLFC at higher loads.
- Completed the analysis of initial DFI proof-of-concept experiments, showing the potential benefits of the technology for sustaining LLFC at engine loads above ~20%. These initial results show that DFI can be highly effective at preventing soot formation over a range of typical diesel engine conditions and does not require an oxygenated fuel.
- Showed that the equivalence ratio at the flame lift-off length and the aromatic content of the fuel correlate much more strongly with soot emissions than the liquid phase fuel penetration length. This result supports the idea that the volatility of a new fuel is less important for soot emissions than its ignition quality and aromatic content.

Future Directions

- Continue to explore DFI to obtain a better understanding of its governing parameters and sensitivities, and to identify the knowledge gaps that should be bridged to enable continued improvement of the technology so that it can be deployed in production engines

- Conduct a modeling study to determine the likely origin(s) of hydrocarbon emissions from conventional mixing-controlled CI combustion; results will have implications as to whether DFI likely holds promise for lowering hydrocarbon emissions and increasing combustion efficiencies in addition to lowering soot emissions
- Overcome problems with fuel solidification and conduct optical engine experiments on the CF target fuel and the set of corresponding diesel surrogate fuels described in the FY 2015 report for this project, to determine the level of surrogate fuel compositional accuracy required to adequately match the target fuel combustion performance
- Further develop a laser-induced incandescence diagnostic that can provide semi-quantitative, planar images of the in-cylinder soot volume fraction distribution and the total in-cylinder soot mass as functions of crank angle. ■

Introduction

This project simultaneously addresses a number of critical transportation energy issues by seeking to enhance domestic energy security by developing high-efficiency, fuel-flexible engine technologies; mitigating environmental impacts by lowering undesired emissions from engines and energy production; and improving the competitiveness of domestic industry through the invention and development of high-performance engine and fuel systems that are cost-effective, sustainable, and durable. The research focuses on mixing-controlled CI combustion due to its inherently high efficiency, power density, fuel flexibility, ease of control, and durability, especially in the heavy-duty sector where battery-powered vehicles face large practical challenges. The goal is to develop full-time, high-efficiency LLFC engines that are tolerant to liquid fuels with the widest possible property ranges. Achievement of the goal would provide clean combustion engines with less costly aftertreatment systems (which currently cost nearly as much as the engine itself) that could operate using a range of low-cost, low-carbon fuels. This would provide options that would benefit the nation, the environment, consumers, engine manufacturers, and energy companies.

Approach

Two approaches were employed to achieve the three major FY 2016 accomplishments listed above for this primarily experimental project. First, the LLFC and liquid length research projects were conducted using

the principal investigator's optical engine lab at Sandia. Two fuels were used in the LLFC study: CF and a blend, denoted T50, containing 50 vol% CF and 50 vol% tripropylene glycol methyl ether (an oxygenate) [1]. Second, the DFI experiments were conducted in Sandia's constant-volume combustion vessel using a single-hole fuel injector, steel and quartz ducts with various geometries, and a non-oxygenated fuel.

Results

Optical engine experiments with a six-hole injector tip sustained LLFC to a maximum load of 6 bar gross indicated mean effective pressure (gIMEP) with the T50 fuel at 240 MPa injection pressure, 30°C intake manifold temperature, 85°C coolant temperature, and +5 crank angle degrees (CAD) after top dead center (ATDC) start of combustion (SOC) timing. The achievement of LLFC was confirmed by independent soot measurements using a smoke meter, spatially integrated natural luminosity (NL) from high-speed in-cylinder imaging, equivalence ratio estimates from in-cylinder 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 achieved under any of the test conditions with CF, indicating that fuel oxygenation is a key enabling aspect of the approach. Selected imaging results for T50 and CF are provided in Figure 1. As evident from the apparent heat release rate and spatially integrated natural luminosity (SINL) results shown in Figure 2, LLFC was also found to be tolerant of charge-gas dilution, which was used to lower engine-out emissions of nitrogen oxides by >90%. Combustion was stable under LLFC conditions, with a coefficient of variation of gIMEP less than 1.5%. Combustion noise and ringing intensity were also 4–6 dBA and 60–80% lower, respectively, for LLFC with T50 relative to using the same operating conditions with CF. LLFC operation at loads higher than ~6 bar gIMEP was not possible without moving beyond the range of realistic engine operating conditions and/or fuel composition, highlighting the need for an additional mixing-enhancement approach such as DFI to enable sustained LLFC at higher loads. Further details can be found in Gehmlich et al. [1].

Investigation of DFI as a means to enhance the fuel/charge-gas mixture in the autoignition zone (see Figure 3 for a schematic) continued in FY 2016. The initial objective of the DFI experiments in Sandia's constant-volume combustion vessel was to inhibit soot formation. The NL images of free-spray vs. DFI combustion provided in Figure 4 show that this objective was achieved across a range of ambient temperatures from 850 K to 1,000 K. The large reduction in NL signal

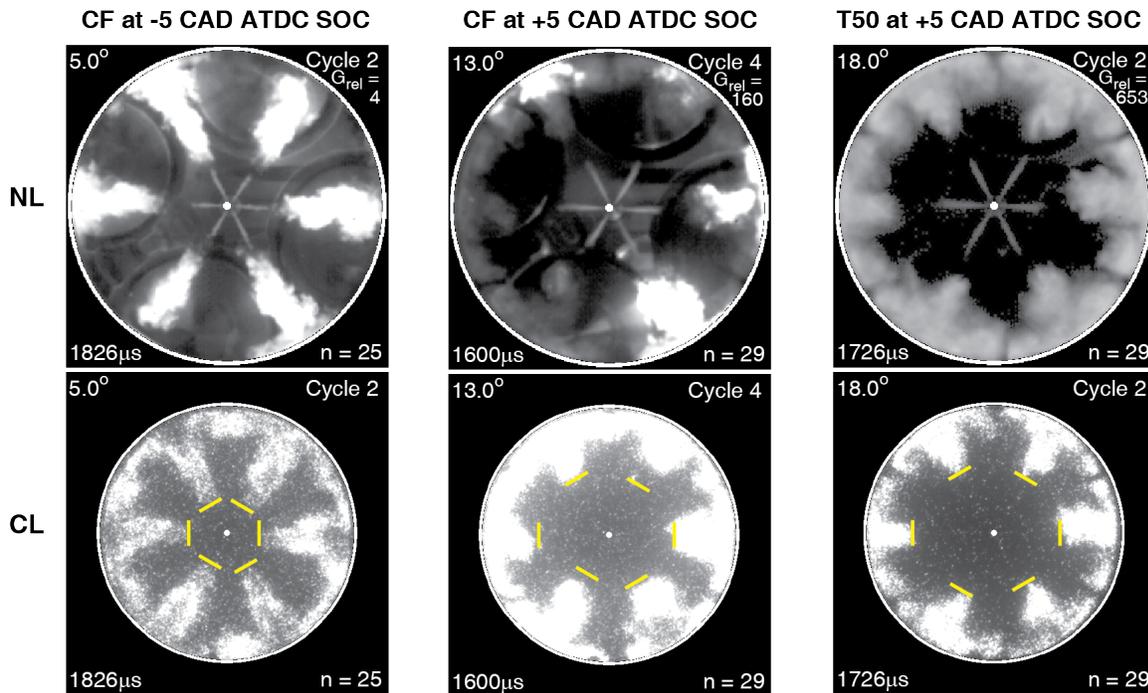


Figure 1. In-cylinder images of NL (top row) and electronically excited hydroxyl-radical (OH^*) chemiluminescence (CL, bottom row) showing the progression from conventional diesel combustion in the left column to LLFC in the right column [1]. Bright NL and OH^* CL signals indicate regions of hot soot and high-temperature chemical reactions, respectively. The image crank angle is shown in the upper left corner of each image frame, and the relative NL camera gain (G_{rel}) is shown in the upper right corner of each NL image frame. It is evident that the peak NL signal levels are approximately three orders of magnitude lower for LLFC, indicating that soot formation has been prevented. In the CL images, each yellow bar indicates the lift-off length for its corresponding spray. The SOC timing was retarded from the left to the middle column, whereas the SOC timing was retarded and the fuel was changed from CF to T50 from the left to the right column. Images were acquired at the crank angle of 70% of fuel mass burned.

is particularly interesting for the 1,000 K case, where it appears that the flame is anchored at (or perhaps even upstream of) the duct exit, so any charge-gas that was available to lower soot formation at the duct exit had to be drawn into the duct within the small, 2-mm gap between the injector orifice outlet and the inlet to the duct. As shown in Figure 5, this 2-mm gap for DFI is much shorter than the ~ 8.5 -mm lift-off length for the free-spray case at 1,000 K. The lower soot for the DFI case at 1,000 K would seem to be due to enhanced mixing within the duct (i.e., a lower centerline equivalence ratio), because entrainment from outside of the duct cannot take place downstream of the duct inlet, so the total amount of entrainment for the 1,000 K DFI case is likely lower than for the corresponding free-spray case. At this point, however, the mixture fields for the DFI vs. the free-spray cases have not been measured, and additional research is required to understand the physical mechanisms underlying the observed success of DFI. Further details can be found in Mueller et al. [2].

Conclusions

- LLFC shows promise as an approach for achieving high-efficiency, fuel-flexible, emissions compliant, low-noise, easy to control, and cost-effective engines for the future.
- Two primary limitations of LLFC are that it currently cannot be achieved at high loads, and an oxygenated fuel is required for it to be sustained even at $\sim 20\%$ load.
- DFI shows promise for overcoming the two primary limitations of LLFC by improving the fuel/charge-gas mixture where autoignition occurs. Even a non-optimal DFI configuration can enable sustained LLFC at ambient temperatures ~ 150 K higher than for conventional free-spray combustion.
- Further research is required to better understand the underlying physical processes contributing to the

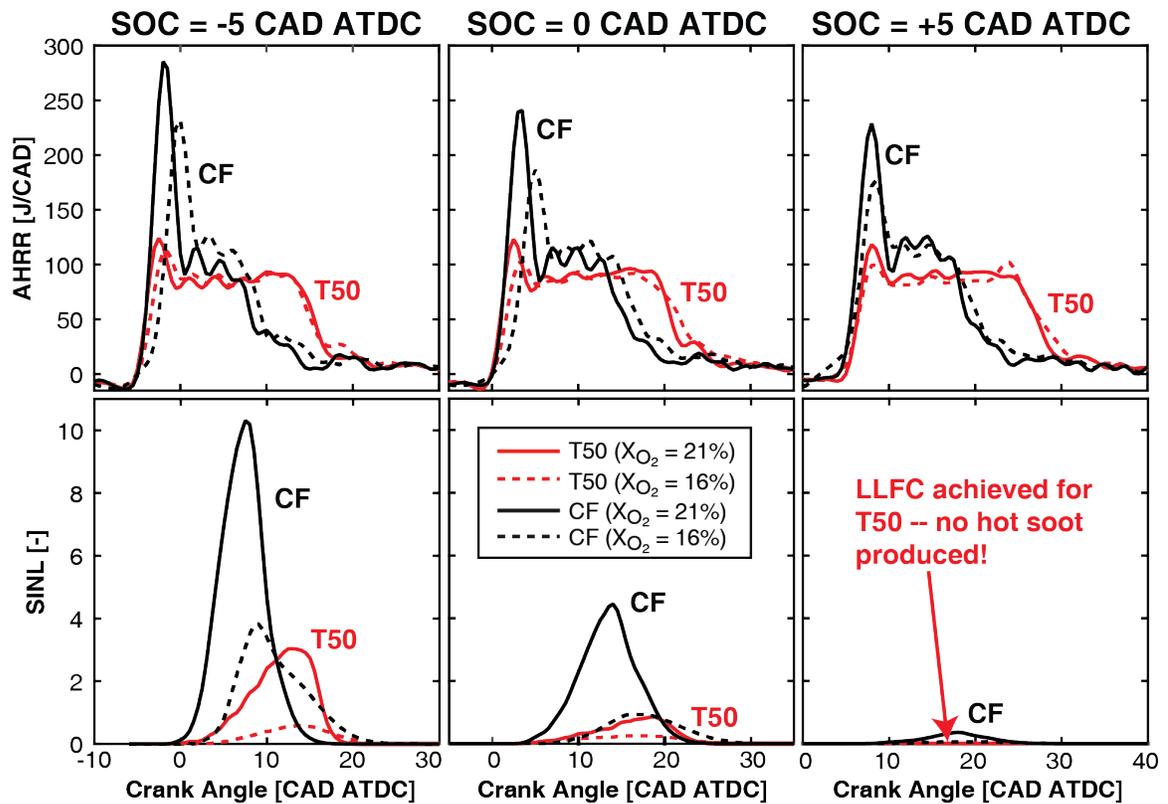


Figure 2. Apparent heat release rate (AHRR, top row) and SINL (indicator of the presence of hot soot, bottom row) showing the progression from conventional diesel combustion in the left column to LLFC for T50 in the right column [1]. LLFC is achieved for T50 for both intake oxygen mole fractions (X_{O_2}) of 21% and 16%.

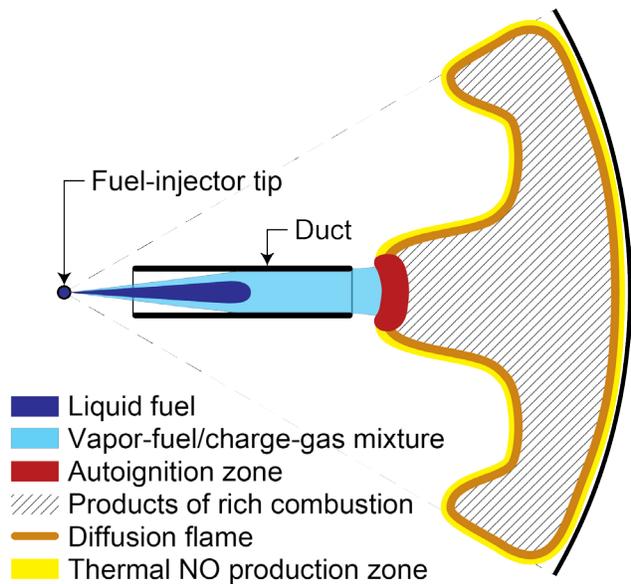


Figure 3. Schematic of the DFI concept on one fuel spray within a CI, direct injection engine

success of DFI so that it can be further developed for deployment in production engines.

- The equivalence ratio at the flame lift-off length and the aromatic content of the fuel correlate much more strongly with soot emissions than the liquid phase fuel penetration length, indicating that the volatility of a new fuel is less important for soot emissions than its ignition quality and aromatic content [3].

References

1. 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 Int. J. Engines* 9(3), 2016, doi:10.4271/2016-01-0730.
2. Mueller, C.J., Nilsen, C.W., Ruth, D.J., Gehmlich, R.K., Pickett, L.M., and Skeen, S.A., "Ducted Fuel Injection: A Technique for Lowering Soot Emissions from Direct-Injection Engines," *manuscript in preparation*, 2016.

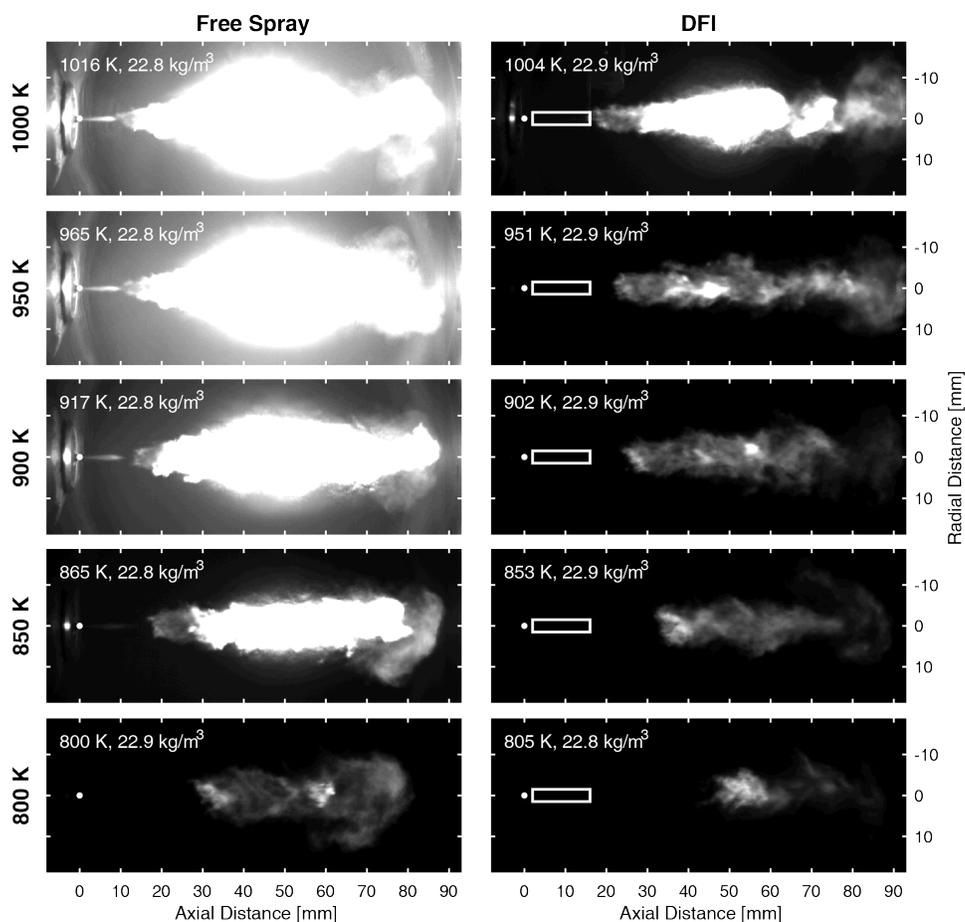


Figure 4. Image frames from NL movies of free-spray combustion (left column) vs. DFI combustion (right column) with a 3-mm inner diameter, 14-mm-long, steel duct positioned 2 mm downstream of the injector orifice exit and collinear with the spray axis. Bright NL signal is an indicator of the presence of hot soot. Identical image exposure parameters were used for all frames. Each row of images corresponds to a different nominal ambient temperature in the combustion vessel, as shown at the far left. The actual ambient temperature and density values are indicated in the upper left region of each image frame. Each displayed image was acquired 3.03 ms after the start of fuel injection. The white dot at the origin indicates the injector orifice exit, and the solid white rectangle in each DFI image indicates the location of the inner diameter of the duct. For all image frames, the fuel was n-dodecane, the injection pressure was 150 MPa, the injector orifice diameter was 90 μm , and the ambient oxygen mole fraction was 21%.

3. 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, doi:10.1021/acs.energyfuels.5b01754.

FY 2016 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* **30**(2):1445–1461, 2016, doi:10.1021/acs.energyfuels.5b02879.

2. Das, D.D., Cannella, W.J., McEnally, C.S., Mueller, C.J., and Pfefferle, L.D., "Two-Dimensional Soot Volume Fraction Measurements in Flames Doped with Large Hydrocarbons," *Proc. Combust. Inst.*, 2016, doi:10.1016/j.proci.2016.06.047.

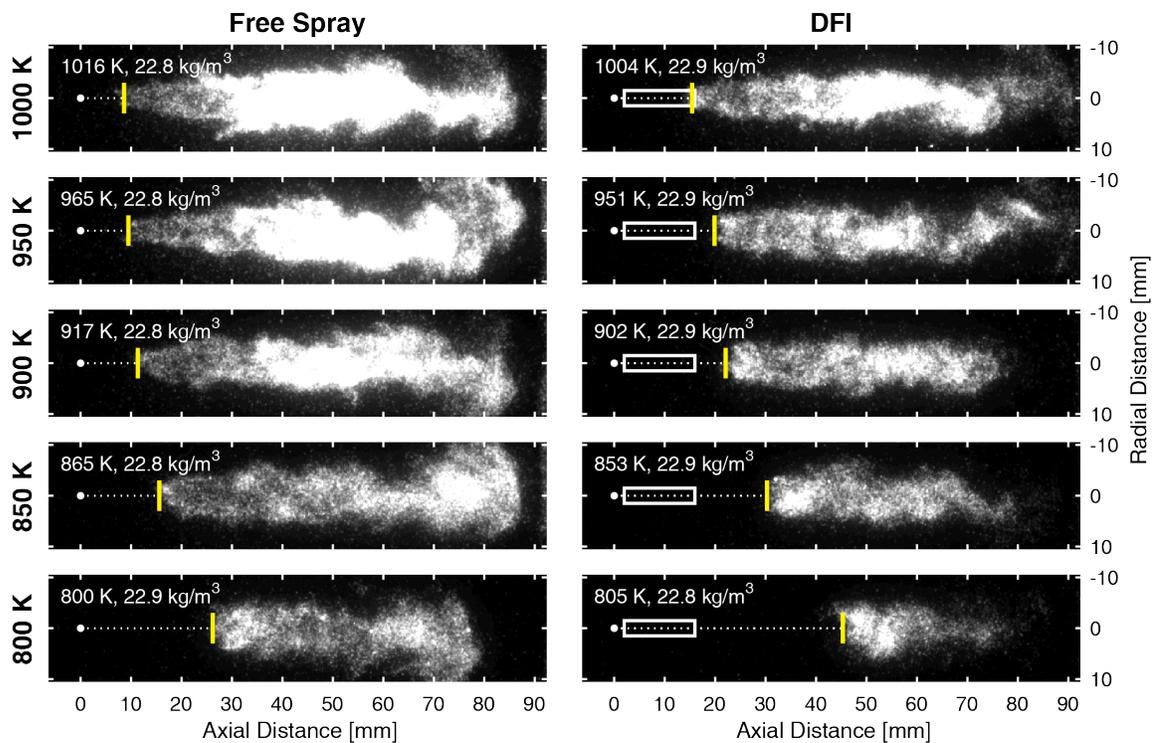


Figure 5. Image frames from OH* CL movies of free-spray combustion (left column) vs. DFI combustion (right column) for the same duct configuration as shown in Figure 4. Bright OH* CL signal is an indicator of the presence of high-temperature chemical reactions. The horizontal dotted line shows the spray axis, and the yellow vertical solid line denotes the flame lift-off length. Each displayed image was acquired 3.08 ms after the start of fuel injection. Other features are as described in the caption of Figure 4.

- Gehmlisch, 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 Int. J. Engines* **9**(3), 2016, doi:10.4271/2016-01-0730.
- 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," *Appl. Therm. Eng.* **101**:639–646, 2016, doi:10.1016/j.applthermaleng.2015.12.068.
- 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, doi:10.1021/acs.energyfuels.5b01754.
- Mueller, C.J., "Improved Fuels and Mixing-Controlled Combustion Strategies for High-Efficiency Compression-Ignition Engines," *Proc. of DOE Advanced Engine Combustion and Fuels Program*

Review, DOE Office of Vehicle Technologies Annual Report, 2015.

- Mueller, C.J., "A Review of the Effects of Fuel PAH Content on PM/Soot Emissions from CI Engines and Vehicles," Report to CI Fuels Roadmap Sub-Group of ACEC Technical Team, October 8, 2015.

FY 2016 Presentations

- Mueller, C.J., "Status Update on AVFL-18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling," Coordinating Research Council Advanced Vehicles, Fuels, and Lubricants Committee Meeting, San Francisco, CA (January 14, 2016).
- Mueller, C.J., "Diesel Surrogate Fuels for Engine Testing and Chemical-Kinetic Modeling: Compositions and Properties," Advanced Engine Combustion Program-Review Meeting, Livermore, CA (February 8, 2016).
- Gehmlisch, 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,” 2016 SAE International Congress and Exposition, Detroit, MI (April 12, 2016).
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, Torrance, CA (May 9, 2016).
 5. McConnell, S.S. and Mueller, C.J., “AVFL-22a: 2nd CRC Advanced Fuels and Engine Efficiency Workshop,” Coordinating Research Council Advanced Vehicles, Fuels, and Lubricants Committee Meeting, Torrance, CA (May 9, 2016).
 6. Miles, P.C., “Co-Optima AED,” DOE Office of Vehicle Technologies Annual Merit Review Meeting, Washington, D.C. (June 6, 2016).
 7. Mueller, C.J., “Recommendations for Co-Optima Thrust II Fuel Properties for Mixing-Controlled Combustion Strategies,” presentation to Co-Optima Leadership Team and LGGF Team Leads, online (July 1, 2016).
 8. Mueller, C.J., “What Do Engines Want for Breakfast?” **invited presentation**, 2016 Sustainable Transportation Summit, Washington, D.C. (July 12, 2016).
 9. Mueller, C.J., “Caterpillar/Sandia Collaborative Combustion Research: Recent Progress and Future Plans,” **invited presentation**, Energy & Transportation Research Collaboration Meeting, Caterpillar Global R&D Headquarters, Peoria, IL (July 21, 2016).
 10. Wang, Y., Gehmlich, R.K., and Mueller, C.J., “Status Update on Vertical LII Diagnostic Development for the Visualization of In-Cylinder Soot Distributions,” Caterpillar Global R&D Headquarters, Peoria, IL (July 21, 2016).
 11. Das, D.J., Cannella, W.J., McEnally, C., Mueller, C.J., and Pfefferle, L.D., “Sooting tendencies of diesels, jet fuels, and their surrogate components,” 36th International Symposium on Combustion, Seoul, Korea (August 1, 2016).
 12. Mueller, C.J., “Recommendations for Co-Optima Thrust II Fuel Properties for Mixing-Controlled Combustion Strategies,” presentation to Co-Optima Low Greenhouse Gas Fuels Team, online (August 8, 2016).
 13. Wang, Y., Gehmlich, R.K., and Mueller, C.J., “Status Update on Vertical LII Diagnostic Development for the Visualization of In-Cylinder Soot Distributions,” Advanced Engine Combustion Program-Review Meeting, Detroit, MI (August 17, 2016).
 14. Mueller, C.J., “Status Update on AVFL-18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling,” Coordinating Research Council Fuels for Advanced Combustion Engines (FACE) Working Group Meeting, Detroit, MI (September 14, 2016).

Awards, Special Recognitions, and Patents Issued/Pending

1. C.J. Mueller received a USCAR Team Award for contributions to the U.S. DRIVE ACEC Fuels Roadmap Sub-Team (May 26, 2016).
2. C.J. Mueller served as co-chair and local host of the 2nd Coordinating Research Council Advanced Fuels and Engine Efficiency Workshop, Livermore, CA (November 1–3, 2016).
3. US Patent Application #14,789,782: “Ducted Fuel Injection.” Filed/pending July 1, 2015.
4. US Patent Application # 15,363,966: “Ducted Fuel Injection.” Filed/pending November 29, 2016.
5. US Patent Application # 15,364,002: “Ducted Fuel Injection with Ignition Assist.” Filed/pending November 29, 2016.

III.6 Small-Volume Fuel Autoignition Tester Development

Overall Objectives

The National Renewable Energy Laboratory will develop a new experimental method for providing early-stage feedback to biofuel production research and development by identifying promising fuel candidates based on prediction of common autoignition metrics.

Fiscal Year (FY) 2016 Objectives

- Design and fabricate a flow reactor that uses 1 mL or less of candidate bioblendstocks to estimate the autoignition behavior; initial experiments will be conducted with reactor operation at 1 atm
- React primary reference fuels (PRFs), which are mixtures of heptane and isooctane; toluene primary reference fuels (TPRF), which are mixtures of heptane, isooctane, and toluene, and mixtures of TPRF with ethanol to cover a large Research Octane Number (RON) and octane sensitivity (S) space; develop a correlation between experimental observables such as species concentrations versus temperature, and fuel autoignition characteristics such as RON and S
- Extend the experimental space to evaluate the autoignition behavior of the same fuels at higher pressures with a stretch goal of reaching 30 atm

FY 2016 Accomplishments

- Completed the design and fabrication of an atmospheric pressure small-volume reactor
- Achieved goal of mapping species profiles across the temperature range (950 K–1,200 K) using 1 mL or less of fuel (typically 0.5 mL or less)
- Determined that the approach using a molecular beam mass spectrometer (MBMS) was not completely adequate to resolve and identify all species and added a gas chromatograph–mass spectrometer (GC-MS) to the system for more definitive analysis of reaction products
- Developed an initial model based on the analysis of PRF and TPRF for the prediction of RON and S (RON predicted to within 12 to 20 octane number units)
- Designed a reactor that can operate under elevated pressures up to 10 atm; initial design failed to hold pressure, and a second more robust design was developed

Gina Fioroni (Primary Contact) and Robert L. McCormick

National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-4475
Email: gina.fioroni@nrel.gov

DOE Technology Development Manager:
Kevin Stork

Future Directions

- Complete an extensive analysis of experimental observables for a larger set of PRF, TPRF, and TPRF–ethanol blends to build an improved RON and S prediction model
- Develop a simple and rapid approach for measuring residence time distribution in the reactor to assist in modeling of the results
- Continue development of a reactor that can operate at higher pressures, with an initial target of operation of 10 atm, but with a goal of reaching 30 atm ■

Introduction

The purpose of this project is to develop a new experimental method for providing early-stage feedback to biofuel production research and development by identifying promising fuel candidates based on autoignition chemistry. The concept is to use a small-scale tubular flow reactor coupled to an MBMS to conduct oxidation reactions using a small volume of reactant under very dilute conditions (an approximately isothermal, plug-flow reactor). Observables such as the temperature for low temperature oxidation initiation, temperature for high temperature oxidation initiation, and concentrations of intermediate and final product species will be correlated with practical autoignition metrics such as RON or S. To accomplish this, results for a set of PRF and TPRF that map RON and S autoignition space will be used to develop a predictive model for RON and S. Octane sensitivity or S, is the difference between the RON and the Motor Octane Number (MON): $S = \text{RON} - \text{MON}$. As S increases at constant RON, the resistance to autoignition increases at lower temperatures, as encountered in modern engines [1,2]. The

standard method to measure RON and MON uses a large volume of fuel (500 mL) and the test is time consuming and expensive. FY 2016 is the first year of this project.

Approach

A quartz tube design was used for both atmospheric and high-pressure reactor applications. The reactor was connected to an MBMS for the analysis of reactant, intermediate, and product species (electron impact with ionization energy of about 22.5 eV). As normally used the MBMS detects stable intermediate species and cannot detect radical species. Several PRFs and TPRFs were run from 950 K up to 1,200 K. The conditions initially investigated were λ of 1 (stoichiometric). A correlation of the reactor data with RON and S was made using the software program Unscrambler, which is a powerful multivariate analysis tool that performs principal component and statistical analysis of complex data sets. The software automates the process by allowing the MBMS data to be imported as a spectrum and uses an algorithm to produce a regression of the spectral data over the temperature range versus RON (or S). This

approach allows tracking of all the intermediate species concentrations versus temperature.

Results

Fabrication of Reactors

Initial studies were conducted at 1 atm. The reactor was designed with an inner tube and outer tube. Fuel is injected as a liquid inside the inner tube into a helium flow where it evaporates and is heated to the desired run temperature. The preheated fuel then joins the annular flow of helium and oxygen at the start of the reaction zone. The entire length of the quartz tube is heated inside a ceramic furnace. Reaction products are drawn directly into the MBMS interface achieving near-real time product analysis. A photograph of the reactor is shown in Figure 1. The reactor is 25 mm in diameter and 78 cm in length. The inner tube is 13 mm in diameter and 53 cm long. Liquid is injected from a syringe pump via a needle whose tip is 18 cm inside the inner tube. The reaction zone, where fuel, helium, and oxygen are allowed to mix is 26 cm in length. Figure 2 shows the temperature profile of the reactor that was measured over our temperature

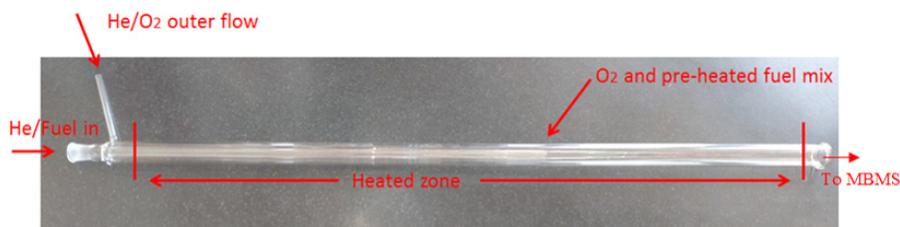


Figure 1. Atmospheric pressure quartz tube reactor

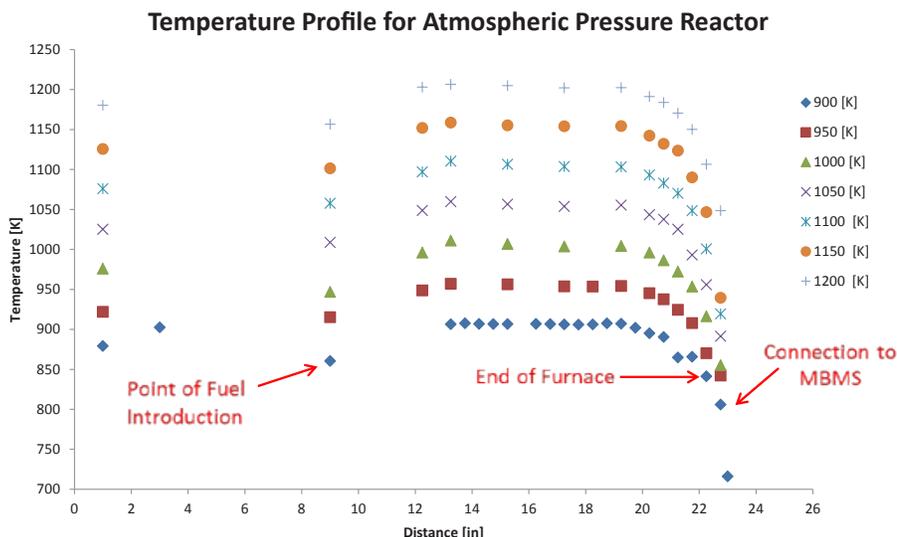


Figure 2. Temperature profile for atmospheric pressure reactor

range of interest. This verifies a consistent temperature across the length of the reactor with a small zone at the connection to the MBMS where the temperature falls off.

For high-pressure experiments, a novel and complex quartz tube reactor with a quartz pressure control valve was designed and custom made. Unfortunately, the quartz pressure control valve could hold the desired pressure at ambient temperature, but would leak once the temperature was increased to 700 K. A complete redesign of the high pressure system was then conducted and this system is currently being fabricated.

PRF and TPRF Model Results

An initial model for prediction of RON was built from PRF runs (PRF0, PRF50, PRF75, and PRF100). Examples of the MBMS spectra utilized in the analysis are shown in Figure 3. The model showed an R^2 of 0.995; however error bars on the predicted values were large. A prediction for S based on TPRFs (TPRF75 [S = 8.7], TPRF95 [S = 4.7], and TPRF100 [S = 11.1]) showed similar results with R^2 of 0.83. A second experimental campaign used an additional three PRFs (PRF25, PRF40, and PRF60) and a triptane standard (a total of eight standards). Doubling the number of standards from four to eight improved the deviation of the RON prediction from 40 RON units to 12–20 RON units. Analysis indicates that on the order of 50+ fuels are needed to build a model with precise prediction capability. A larger fuel matrix intended to

test a much larger RON and S space was designed and will be investigated in FY 2017. These include adding TPRF as well as TPRF blended with ethanol at 10% to 90%. Figure 4 shows the range of RON and S being investigated. Identifying standards that have a low RON, but a high S is challenging, but this space could be further expanded if these standards are identified.

Intermediate Species Observed in PRF and TPRF Experiments

Several intermediate species were observed to form in the PRF and TPRF experiments. Figure 5 shows some of the species observed for isooctane and their concentration (as MBMS total ion current) versus temperature. Table 1 lists the most abundant species observed for isooctane and heptane. Comparing the species observed to species predicted by known reaction mechanisms in the literature for heptane and isooctane shows that we detect several expected species [3,4].

Tubular flow reactors have been used by others [5–7] to investigate reaction mechanisms for autoignition and the reactor described here may also be used for this purpose. Additionally, we unexpectedly observed the formation of soot precursor compounds for some reactants. If we could extend the utility of our system to generate reaction mechanisms for different molecules without a known reaction mechanism, this could be highly beneficial for the Co-Optimization of Fuels & Engines program as we

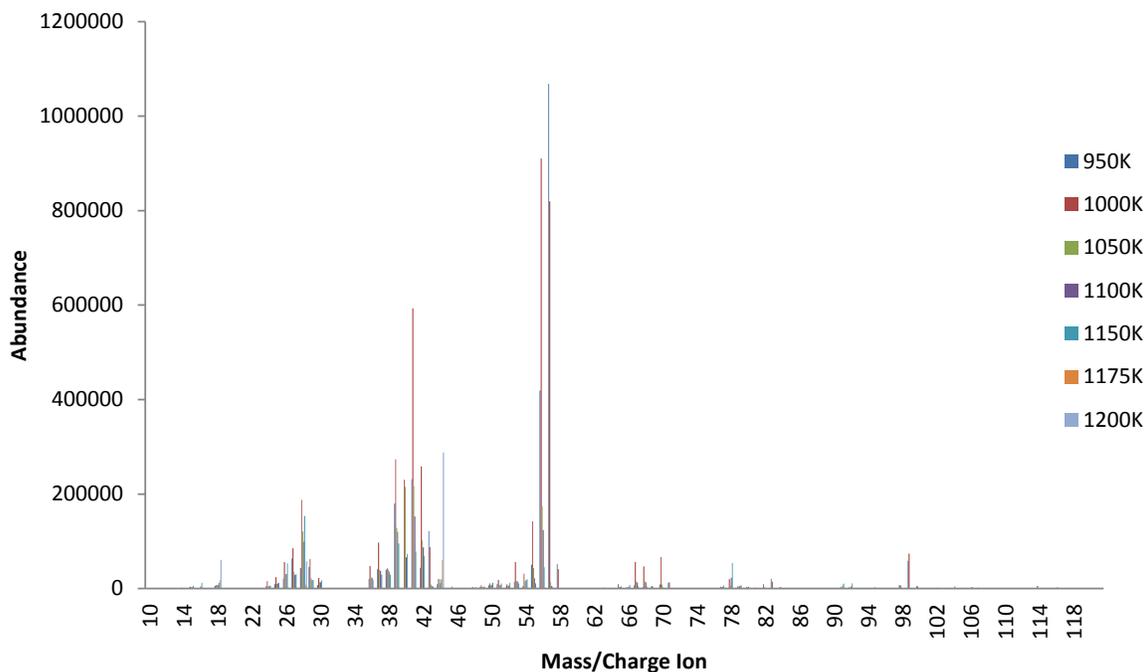


Figure 3. Example mass spectrum for isooctane imported into Unscrambler software

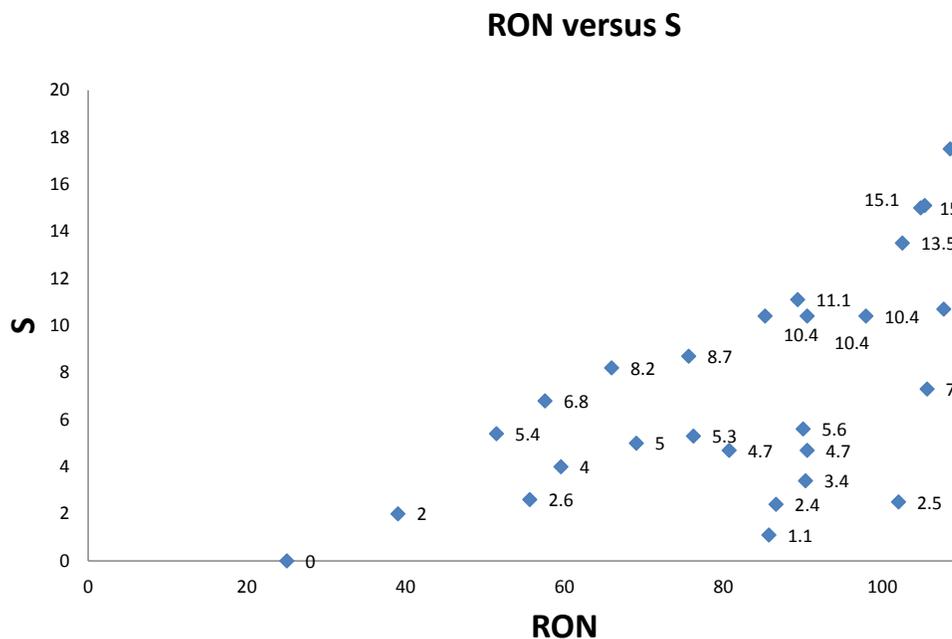


Figure 4. RON versus S for reference fuels to be included in the predictive model

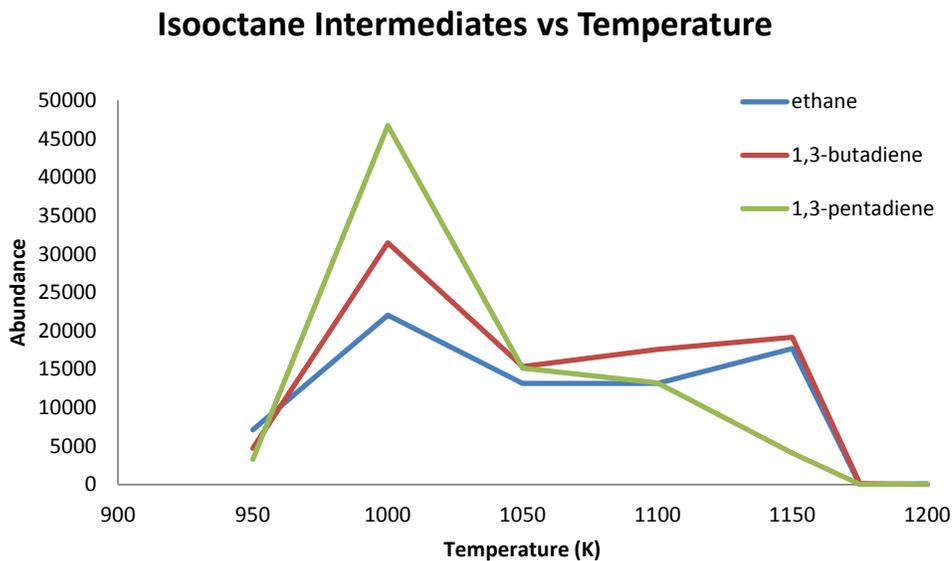


Figure 5. Intermediates versus temperature for isooctane reaction

can rapidly generate detailed information about promising molecules using only a small amount of material. We could potentially compare our laboratory results to modeling results produced by other teams to help validate their reaction mechanisms.

Improvements to Experimental Methodology and Design

One drawback to the MBMS is that it provides a mass spectrum of the entire reaction product mixture. This is not completely adequate to resolve and identify all species present. For example, the ion with mass 28 could correspond to ethylene, carbon monoxide, or

Table 1. Intermediates Observed for Isooctane and Heptane Reaction

Compound ID	Mass Ion
CO,CO2	28,44
ethylene	28
ethane	30
propene	42
butene	56
1,3-butadiene	54
2-methyl-1-butene	56
1,3-pentadiene	68

nitrogen. As a complementary method we have added a GC-MS to the system. Advantages of GC-MS are superior quantitation and positive identification and separation of the intermediate species observed. Species such as ethylene, carbon monoxide, and nitrogen can be separated, positively identified, and quantitated accurately. One potential drawback to the GC-MS is that it does not provide real time analysis. Secondary reactions, such as coupling or degradation of intermediates could potentially occur. Initial GC-MS experiments, for example, used gas sampling canisters where the sample may sit for 24 h prior to analysis. This is not ideal and currently we are building an inline GC sampling valve that can pull a sample directly from the reactor and immediately inject

it into the GC. Combination of the two techniques will strengthen our predictive model for RON and S.

An improved high-pressure reactor design is being developed. Figure 6 shows the concept of the new design that will be fabricated and tested in FY 2017. The new design consists of a similar quartz tube, but will use ultra-torr fittings on the ends held in place with metal plates connected to tensions rods to maintain pressure. These fittings may be water cooled if needed. A metal back pressure regulator will control reactor pressure and feed directly into the MBMS. Some additional calculations of flow in the reactor are being conducted before exact dimensions are finalized.

Conclusions

- An atmospheric pressure reactor was designed and fabricated that uses a very small amount of fuel (<1 mL) to map species profiles across the temperature range 950–1,200 K.
- Experiments were completed that measure fuel autoignition products across this temperature range for several reference fuels, and a promising model for prediction of both RON and S was built.
- An unexpected result was the observation of soot precursor materials noted for aromatics, suggesting the use of the flow reactor for determining reaction mechanisms in a future project.
- The addition of a GC-MS as an analysis method will allow for the separation and positive identification of convoluting species observed in the MBMS.

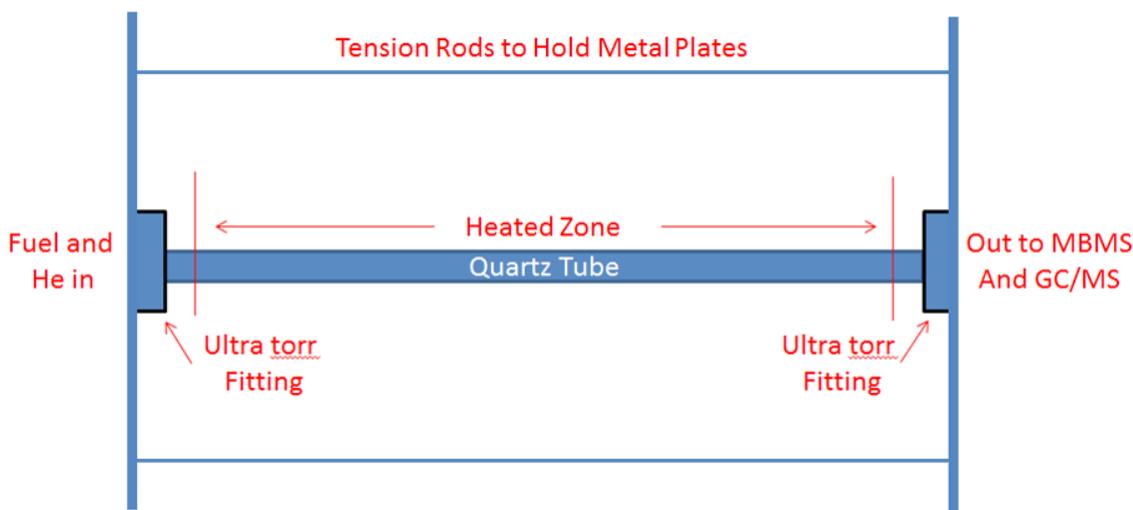


Figure 6. Diagram of new high pressure reactor design

References

1. Kalghatgi, G. *Fuel-Engine Interactions*. Detroit, SAE International, 2013.
2. Leone, T.G., Anderson, J.E., Davis, R.S., Iqbal, A., Reese, R.A., Shelby, M.H., and Studzinski, W.M. 2015. "The Effect of Compression Ratio, Fuel Octane Rating, and Ethanol Content on Spark-Ignition Engine Efficiency." *Environ. Sci. Technol.* 49, 10778–10789.
3. Herbinet, O., Husson, B., Serinyel, Z., Cord, M., Warth, V., Fournet, R., Glaude, P.-A., Sirjean, B., Battin-Leclerc, F., Wang, Z., Xie, M., Cheng, Z., Qi, F., "Experimental and Modeling Investigation of the Low-Temperature Oxidation of n-Heptane," *Combust. and Flame*, 159, 2012, 3455–3471.
4. Slavinskaya, N.A., Starik, A.M., "Kinetic Mechanisms of Ignition of Isooctane-Air Mixtures," *Combustion, Explosion, and Shock Waves*, 40, 2004, 36–56.
5. Beerer, D.J., McDonell, V.G., "An Experimental and Kinetic Study of Alkane Autoignition at High Pressures and Intermediate Temperatures," *Proc. Combust Inst.*, 33, 2011, 301–307.
6. Hori, M., Nakamura, H., Tezuka, T., Hasegawa, S., Maruta, K., "Characteristics of n-Heptane and Toluene Weak Flames in a Micro Flow Reactor with a Controlled Temperature Profile," *Proc. Combust. Inst.* 34, 2013, 3419–3426.
7. Mehl, M., Faravelli, T., Giavazzi, F., Ranzi, E., Scorletti, P., Tardani, A., Terna, D., "Detailed Chemistry Promotes Understanding of Octane Numbers and Sensitivity," *Energy & Fuels*, 20, 2006, 2391–2398.

FY 2016 Publications/Presentations

1. McCormick, R.L., Fioroni, G. NREL Small-Volume Tester – Informal Update, presentation to Co-Optima Program Leadership Team, July 20, 2016.

III.7 Small Volume Autoignition Tester

Overall Objectives

Argonne National Laboratory will develop the capability, using a rapid compression machine (RCM)-based device, to experimentally quantify and thereby rank the autoignition properties for a wide range of high and low octane fuels using very small fuel quantities (<1 mL).

Fiscal Year (FY) 2016 Objectives

- Formulate a new experimental testing protocol whereby RCM results can be directly correlated to conventional, spark ignition (SI)-based octane ratings, and thereby facilitate fuel rankings with the potential to facilitate extend the correlations to advanced compression ignition (ACI) engine-based metrics, where these may include boost, equivalence ratio (ϕ), and dilution sensitivities
- Draft a preliminary design for a new RCM configuration that can drastically reduce the fueling requirements relative to Argonne's twin-piston RCM and significantly increase the throughput for the measurements

FY 2016 Accomplishments

- A new testing protocol was conceived and validation tests conducted using a range of primary reference fuel (PRF) and toluene reference fuel (TRF) blends at thermodynamic conditions typically experienced in the ASTM octane rating test protocol, as well as beyond
- The autoignition measurements of the PRF blends were successfully correlated to trends observed at Research Octane Number (RON) test conditions
- Design constraints were established to scale-down the RCM geometry in order to reduce the fueling requirements, while at the same time increasing the throughput of the device to achieve the target goals

Future Directions

- Additional measurements and insight are necessary in order to understand differences between the two different octane rating tests, i.e., RON and Motor Octane Number (MON), and how the autoignition measurements in an RCM-based device can be extended beyond the initial correlation of the PRF blends at the RON conditions.

S. Scott Goldsborough

Argonne National Laboratory (ANL)
9700 S. Cass Avenue
Bldg. 362
Argonne, IL 60439
Phone: (630) 252-9375
Email: scott.goldsborough@anl.gov

DOE Technology Development Manager:
Kevin Stork

- Fuels beyond the initial surrogate fuel matrix should be employed in order to quantify the influence of sensitivity (i.e., $S = \text{RON-MON}$) within the new testing protocol.
- The approach to utilize a scaled-down RCM to evaluate potential future fuels has demonstrated good promise with the possibility of extending the measurements to future ACI fuel metrics and a prototype should be fabricated and commissioned. ■

Introduction

Fuel performance in modern SI and ACI engines depends on many factors. Although autoignition chemistry is a primary driver, heat of vaporization and flame speed as well as chemical kinetic sensitivities to thermal and compositional stratification, are also important. Furthermore, the development and propagation/amplification of pressure waves after localized autoignition events, which can lead to structural damage, can also be dependent on the properties of the fuel [1]. Conventional test protocols and fuel ratings convolve many of these factors and thus it is difficult to discern which fuel properties are most important, and to quantify the influence of each on engine performance. Additionally, there are no commercial devices or established experimental protocol that can be used to experimentally measure the autoignition properties for a wide range of high and low octane fuels using very small fuel quantities (<1 mL). Standardized ASTM protocols typically employed with the Cooperative Fuels Research, variable compression ratio engine can require nearly 1 L of fuel for the two test schedules, i.e., RON and MON. Modern and future high performance engines operate at conditions that are not directly represented by

the conventional RON and MON tests and so this is a limitation for understanding how new fuels will behave in these configurations. Methodologies to augment RON and MON ratings are under investigation [2], but the utility of such modifications is not completely clear. Towards the development and vetting of new fuels and their co-optimization with advanced SI and ACI engines, a small volume autoignition tester that can facilitate the ranking of potential engine performance would have great benefit.

Approach

The approach used in this project is based on ANL's Rapid Compression Machine facility, where this device is able to access experimental conditions that are directly relevant to modern SI and ACI engines, e.g., $T = 650\text{--}1,100\text{ K}$, $P = 10\text{--}100\text{ bar}$, $O_2 = 10\text{--}21\%$, $\phi = 0.2\text{--}3.0$. ANL's RCM typically uses 5–20 mL of fuel to conduct tests over a wide range of conditions, with the autoignition chemistry studied over the low-temperature, negative temperature coefficient, and intermediate-temperature regimes.

RCMs have been used for nearly 100 years to investigate autoignition phenomena at engine-relevant conditions [3–4], where Livengood and Wu [5] were one of the earliest groups to quantitatively demonstrate direct correlations between measurements within these fixed temperature and pressure devices to observations in internal combustion engines via their so-called, knock integral. Fuel chemistry is significantly dependent on the thermodynamic and mixture conditions where rates and extents of oxidation via low-temperature, negative temperature coefficient and intermediate-temperature kinetic pathways can be substantially altered, e.g., through intake boosting systems. Complex non-linear behavior exists making it difficult to extrapolate measurements from ambient (e.g., $P = 1\text{ bar}$), or extremely dilute (e.g., $<1\% O_2$) to engine-relevant conditions. One advantage to an RCM-based approach is the capability to acquire data at these conditions, while this configuration is capable of easily isolating autoignition properties that are convoluted in engine-based approaches.

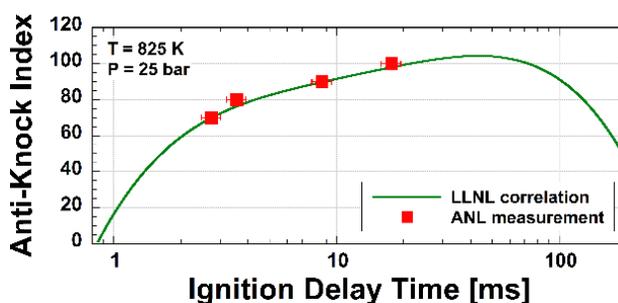
Results

Autoignition measurements were conducted over a wide range of conditions covering fuel reactivity, temperature, and pressure. PRFs and TRFs were used with RON values ranging from 60 to 100, and sensitivities from 0 to 12. More than 700 tests were conducted during the experimental campaign with temperatures ranging from 700 K to 1,000 K and pressures from 10 bar to 50 bar. Stoichiometric fuel:air loading was utilized with a dilution level of nearly 6% by mass, i.e., 18.5% O_2 (by mole).

These operating conditions are representative of those found in the in the RON test schedule.

Figure 1 illustrates measured ignition delay times at a single temperature and pressure condition ($T = 825\text{ K}$, $P = 25\text{ bar}$), along with the Anti-Knock Index correlation developed in Mehl et al. [6]. It should be noted that the correlation depicted here was derived based on a chemical kinetic model with constant volume simulations conducted at $T = 825\text{ K}$ and $P = 25\text{ bar}$. Fairly good agreement is observed between the measurement and the correlation. Figure 2 next illustrates the results of a new correlation parameter that is derived from the ANL autoignition measurements and this is plotted against RON for four of the PRF mixtures. The correlation parameter (ξ) employs a new testing protocol which may be able to yield an octane rating on the order of ± 0.5 . This will be discussed in detail in a forthcoming publication.

The existing RCM facilities at ANL are not capable of achieving small-volume fueling at the targeted level due to the large size of the reaction chamber (50.8-mm bore



LLNL – Lawrence Livermore National Laboratory

Figure 1. Correlation between Anti-Knock Index and ignition delay time at specified temperature ($T = 825\text{ K}$) and pressure ($P = 25\text{ bar}$)

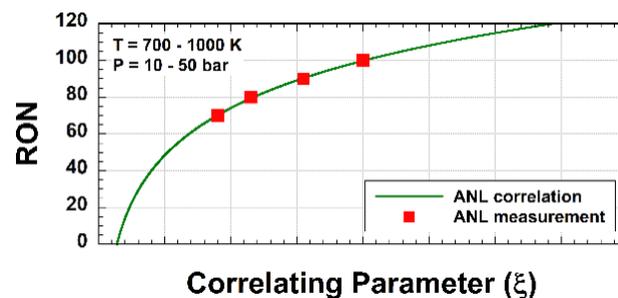


Figure 2. RON and RCM measured parameter (ξ) covering a range of conditions relevant to the RON test as well as modern SI and ACI engines

x 300-mm stroke) and the size of the mixture preparation tank (5.6 L). A new machine will need to be designed, fabricated, and commissioned for this purpose. A concept and preliminary design which is configured to utilize the new operating protocol have been pursued as part of the FY 2016 task, where a bore on the order of 15 mm with a stroke of ~45 mm is expected to be sufficient. Techniques have been devised to minimize the influence of high surface areas at these scales.

Work in future fiscal years should conduct additional measurements to understand differences between the two different octane rating tests, i.e., RON and MON, and how the autoignition measurements in an RCM-based device can be extended beyond the initial correlation of the PRF blends at the RON conditions. Furthermore, additional fuels beyond the initial surrogate fuel matrix should be utilized to quantify the influence of sensitivity (i.e., $S = \text{RON} - \text{MON}$) within the new testing protocol.

Conclusions

- A new testing protocol was conceived and validation tests conducted using a range of PRF and TRF blends, where the PRF blends were successfully correlated to trends observed at RON test conditions.
 - Design constraints were established to scale-down the RCM geometry to reduce the fueling requirements and increase throughput of the device to achieve the target goals.
 - Additional measurements and insight are necessary to understand differences between the two different octane rating tests, i.e., RON and MON, and how the autoignition measurements in an RCM-based device can be extended beyond the initial correlation of the PRF blends at the RON conditions.
- The approach of utilizing a scaled-down RCM to evaluate potential future fuels has demonstrated promise with the possibility to extend the measurements to future ACI fuel metrics and a prototype should be fabricated and commissioned.

References

1. L. Bates, D. Bradley, G. Paczko, N. Peters, "Engine hot spots: modes of auto-ignition and reaction propagation," *Combust. Flame* 166 (2016) 80–85.
2. G. Kalghatgi, "Auto-ignition quality of practical fuels and implications for fuel requirements of future SI and HCCI engines," SAE Paper 2005-01-0239, 2005.
3. C.-J. Sung and H.J. Curran, "Using rapid compression machines for chemical kinetics studies," *Prog. Energy Comb. Sci.* (44) 1–18, 2014.
4. S.S. Goldsborough, D. Longman, M.S. Wooldridge, R.S. Tranter and S. Pratt, "1st International RCM Workshop Meeting Report," August 28–29, 2012.
5. J.C. Livengood and P.C. Wu, "Correlation of autoignition phenomena in internal combustion engines and rapid compression machines," *Symp. (Int.) Combust* 5 (1955) 347–356.
6. M. Mehl, J.Y. Chen, W.J. Pitz, S.M. Sarathy and C.K. Westbrook, "An approach for formulating surrogates for gasoline with application toward a reduced surrogate mechanism for CFD engine modeling," *Energy Fuels* 25 (2011) 5215-5223.

III.8 The Microliter Fuel Ignition Tester (μ FIT): Creating a High Throughput Measurement Process for Small Sample Volumes

Overall Objectives

- Accelerate the discovery of high performance transportation fuels by developing a measurement process that rapidly screens small sample volumes based on their expected engine performance
- Demonstrate experimental and computational procedures that can screen at least 100 new fuel blends in a month using a sample size less than 20 μ L
- Measure the accuracy and repeatability of the new screening process to predict traditional combustion performance measurements that are directly related to the engine operation (e.g., Research Octane Number [RON], Motor Octane Number [MON], and flame speed)

Fiscal Year (FY) 2016 Objectives

- Demonstrate the Microliter Fuel Ignition Tester (μ FIT) measurements are sensitive to the fuel composition
- Verify that the ignition and extinction temperatures measured in μ FIT are correlated with reactivity of the fuel
- Measure the wall temperature in μ FIT and quantify its uncertainty to enable detailed chemical kinetic modeling of the unsteady flame dynamics
- Create a detailed thermal model of μ FIT to relate the observed thermocouple temperature to the wall temperature needed for the flame model and the derived fuel property metrics

FY 2016 Accomplishments

- Completed μ FIT measurements for three primary reference fuel (PRF) blends to show that the device has sufficient sensitivity to the fuel composition, and that the ignition and extinction temperatures are correlated to the fuel reactivity
- Developed a detailed thermal model of μ FIT that includes temperature dependent material properties and non-gray body radiation for the quartz tube and thermocouple

Matthew McNenly (Primary Contact), Christopher Walton, and Nicholas Killingsworth

Lawrence Livermore National Laboratory (LLNL)
7000 East Ave. (L-140)
Livermore, CA 94550
Phone: (925) 424-6418
Email: mcnenly1@llnl.gov

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Ingmar Schoegl, Louisiana State University,
Baton Rouge, LA

- Created and tested an improved wall temperature measurement technique that increases the accuracy beyond what is attainable with a thermocouple

Future Directions

- Develop a detailed chemical kinetic model of the unsteady flame dynamics in the μ FIT system using LLNL's high performance chemistry solver Zero-RK
- Validate the adiabatic laminar flame speed predictions made using the μ FIT measurements combined with unsteady flame simulations
- Measure small volume fuel samples for the High Performance Fuels Team within the Co-Optimization of Fuels & Engines (Co-Optima) program
- Extension beyond the current scope of the experimental research was selected for contract negotiations for the Co-Optima University Call (DE-FOA-0001461) ■

Introduction

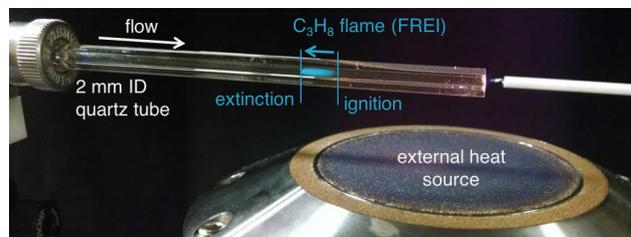
The high cost of current methods to measure engine relevant combustion properties impedes the discovery of new fuel blends. Traditional ASTM standard fuel property measurements for RON and MON can be conducted at third party testing facilities for a modest cost (\$100–\$200

per sample) and high bandwidth (hundreds per month). However, they require a relatively large sample, typically 800 mL per test. This large volume adds significant production or procurement costs in terms of dollars and time to consider any new blend candidate. In contrast, rapid compression machine and shock tube experiments can provide the ignition characteristics of a fuel at engine relevant pressures using small samples (less than 10 mL in some devices). The throughput of these canonical experiments is relatively small, on the order of ten blends per month under ideal circumstances, and at a much higher cost than the ASTM tests. Further, both approaches suffer from having high capital costs for new installations, on the order of a few hundred thousand dollars or more (excluding labor), which limits the growth of the national (or global) testing bandwidth.

The overall objective is to reduce the barriers to evaluating new fuel blends based on their expected engine performance. Specifically, the performance target for the screening bandwidth is at least one hundred new fuel blends in a month, and the target for sample size is less than 20 μL . The new device must also be less than \$200,000, which is an approximate lower bound on the equipment costs for a new rapid compression machine or Cooperative Fuels Research engine. These targets were identified by the leaders of the High Performance Fuels Team in the Co-Optima program. If met, the search for high-quality fuel blends from both fossil and bio-derived sources is expected to accelerate dramatically.

Approach

The first prototype of the μFIT is shown in Figure 1. It is based on an existing combustion experiment that has a relatively low equipment cost and is capable of handling



ID - inside diameter

Figure 1. Experimental setup for μFIT operating with a propane and air flame in the unsteady FREI mode. The time needed for the flame to propagate from the ignition point to the extinction point is much less than the exposure time resulting in the appearance of a broad flame.

very small sample volumes. Specifically, the millimeter-scale flow reactor studied by Maruta et al. [1] for the past decade is selected as a starting point because it operates at tens of nanoliters per second, costs less than \$50,000 to build new, and has demonstrated, at least qualitatively, that it can detect the presence of low temperature combustion, see Hori et al. [2] for an example. The aim of this project is to develop the measurement and analysis process to predict quantitatively engine relevant fuel properties in less than 15 min, which would enable both the throughput and sample size targets to be met. It should be noted that the actual cost to construct the first μFIT prototype in this project was a small fraction of a new device cost because most of the components were reused from past experiments.

The approach of μFIT differs from Hori et al. [2] in that the unstable FREI regime (Flames with Repetitive Extinction and Ignition) is observed. More specifically, the stability transition from the FREI regime to the higher speed stationary flame is measured instead of the lower speed, weak flame regime. This approach allows for much shorter run times because it does not rely on long camera exposures to resolve the chemiluminescence in a weak or cool flame. Since the FREI cycle typically occurs at 20–200 Hz, the ignition and extinction points can be detected with only tens of nanoliters of fuels at each fuel–air ratio and flow velocity. Further, the μFIT design has shown that the ignition and extinction events can be detected using a low-cost microphone. This means that future designs may not even depend on a camera leading to further reductions in complexity and cost. The observed flame dynamics in μFIT are found to correlate to the high temperature auto-ignition, low temperature heat release, flame speed and extinction properties for known fuels. Two major tasks are pursued in this project to go from these qualitative correlations to quantitative fuel property measurements: (1) increase the sensitivity and accuracy of the experimental measurements, and (2) develop high fidelity simulations to improve the design of the experiment and derive engine relevant fuel property estimates (e.g., flame speed, ignition delay, RON, and MON) from indirect observations of the flame dynamics.

Results

The project made progress on the two major tasks in FY 2016 to support the overall goals of the Co-Optima program, which is partially funded under the Fuel and Lubricant Technologies subprogram in the Vehicle Technologies Office:

- Task 1: Increase the sensitivity and accuracy of the experimental μFIT measurements

- Task 2: Develop high fidelity simulations of the μ FIT experiment

Task 1

Proof-of-concept measurements were conducted with three PRF mixtures: 100% n-heptane, 50% n-heptane and iso-octane, and 100% iso-octane. They produced clear evidence that the μ FIT system has the potential to estimate fuel properties with very small sample volumes. In Figure 2, the ignition (red = T^+) and extinction (blue = T^-) temperatures of the three blends are plotted as a function of the mass-averaged inlet velocity. The transition from the unsteady FREI mode to a stable flame is indicated by the sudden change in the wall temperature difference between ignition and extinction. Initial results show a nearly linear relationship between RON (or MON) and the wall temperature at extinction, where the slope is assessed as 1.0 K to 1.5 K per unit RON based on a curve fit of multiple tests at a given pressure. With improved liquid fuel delivery, the uncertainties in the curve fits are expected to be less than 5 K, which would translate into RON estimates within 3–5 octane numbers. Better accuracy is also expected by collecting measurements at multiple pressures. The flame speeds at the extinction points reveal a similar linear trend. Slopes up to 30 K per cm/s indicate that errors of less than ± 1 cm/s appear readily achievable in the current design. A suitable theoretical framework to compensate for non-adiabatic effects is being developed in FY 2017.

It is crucial that the local wall temperature can be determined for a given flame position. Without an accurate relationship, it is not possible to go beyond the qualitative assessment of fuel reactivity obtained by the

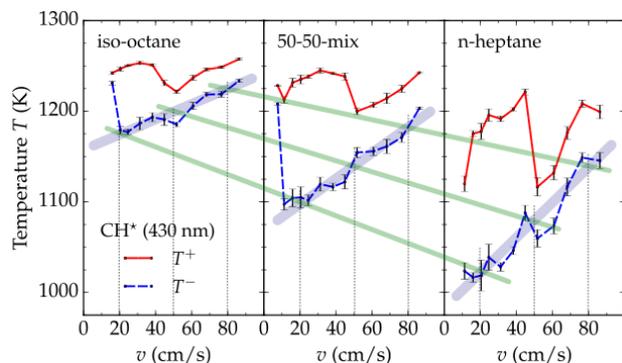


Figure 2. Ignition (red = T^+) and extinction (blue = T^-) temperatures as a function of the mass-averaged inlet velocity for three PRF mixtures. The green lines illustrate that the extinction temperature at a given velocity appears to increase linearly with increasing iso-octane fraction.

original flow reactor design in literature to a quantitative assessment of engine relevant fuel properties. The local wall temperature is essential to compare the ignition and extinction properties of different fuels, as well as the derived metrics for RON and flame speed. In FY 2016, one major challenge was reducing the uncertainty of the temperature calibration, which required substantial effort. In the original experimental procedure, temperature calibrations were obtained by translating a thermocouple within the narrow quartz tube without the flame present. Figure 3 shows the temperature deviations due to transient effects for two thermocouple diameters and various translation speeds, where maximum deviations of ± 45 K were found in the region with steep temperature gradients. While transient effects can be compensated by a numerical correction model to within ± 5 K, results from nominally identical thermocouples reveal unacceptable uncertainty (up to ± 50 K). The larger uncertainty in repeated experiments is attributed to variations in thermocouple placement and manufacturing tolerances. These variations make it difficult to determine the wall temperature with sufficient accuracy to use detailed chemically reacting flow simulations to extract the derived metrics for RON and flame speed.

To overcome this difficulty, an alternative measurement technique based on two-wavelength pyrometry was implemented. This approach uses temperature-dependent black-body emission, which captures optical images with suitable filters in the near infrared range (600–1,000 nm).

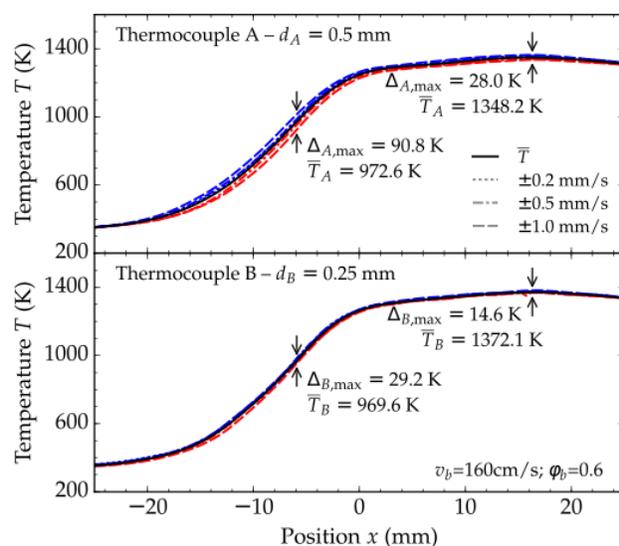


Figure 3. Variation in the uncorrected thermocouple calibration measurements as a function of sheath diameter, translation speed, and direction (red: cold to hot, blue: hot to cold)

The approach is technically calibration free, where preliminary measurements show promising results as illustrated in Figure 4. Post-processed data indicate an anticipated measurement precision of less than 10 K, which is within the range needed for accurate fuel property estimation.

Task 2

A detailed thermal model of the μ FIT experiment was created to quantify the difference between the apparent thermocouple measurement and the true wall temperature when the thermocouple is removed. The model includes temperature-dependent properties for the quartz tube, thermocouple and interior gas. It also includes thermal radiation from the quartz tube (non-gray body) and the thermocouple (gray body). Transient simulations uncovered that the time constant for the thermocouple is about 7 s, see Figure 5. Further, the presence of the thermocouple causes the measured temperature gradient to be less than the true temperature gradient, see Figure 6. These model results indicate that the original translation speed was too fast, which was subsequently confirmed by the experiments shown in Figure 3. In FY 2017, the model will be combined with an unsteady flame dynamics model built using LLNL's Zero-RK software to explore design changes (e.g., external heat source, tube geometry, operating pressure) to further increase the accuracy, sensitivity, and range of applicability of μ FIT.

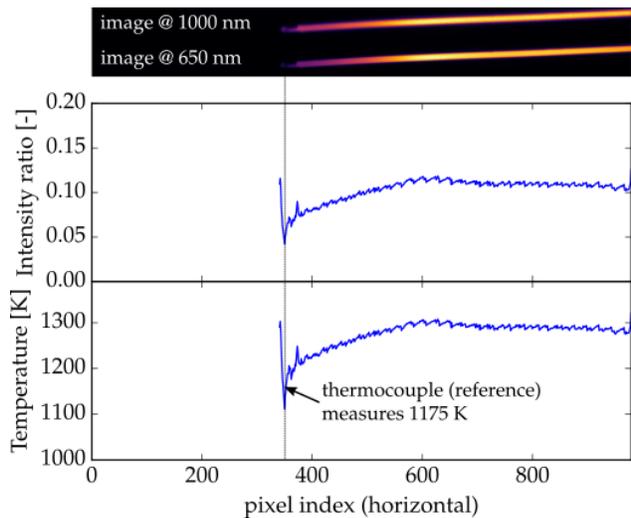


Figure 4. Illustration of the two-wavelength pyrometry technique based on processed images of a thermocouple in μ FIT: (top) filtered false-color images of the thermocouple, and (bottom) post-processed results

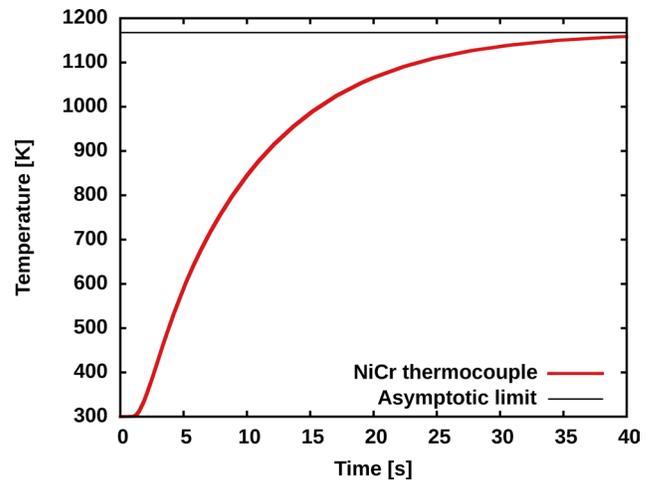


Figure 5. Transient response of the thermocouple when suddenly inserted into the narrow quartz tube. The time constant is approximately 7 s, which indicates that there is an appreciable temperature lag when translating the thermocouple at the original speed of 1 mm/s.

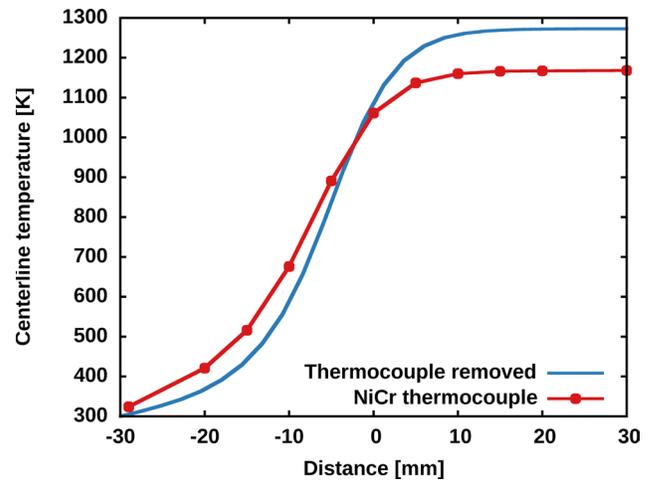


Figure 6. Simulation of the observed centerline temperature (red: with the thermocouple inserted in the tube) and the true centerline temperature during μ FIT operation (blue: thermocouple removed)

Conclusions

In FY 2016, this project advanced toward the development of an experimental process that can rapidly screen small sample volumes based on their expected engine performance. Key achievements included:

- The completion of measurements for three PRF blends, which demonstrated that the device has sufficient sensitivity to the fuel composition, and that the ignition and extinction temperatures are correlated to the fuel reactivity.
- The creation of a detailed thermal model that includes temperature-dependent material properties and non-gray body radiation. The thermal model simulations subsequently led to the correction of a major error in the wall temperature measurement with the thermocouple.
- The development and initial validation of an improved wall temperature measurement technique that increases the accuracy and precision well beyond what is achieved with a thermocouple.

In FY 2017, the project will focus on validating the improvements to the temperature measurements, quantifying the uncertainty in the flame speed measurements, and preparing μ FIT to process real-world samples from the High Performance Fuels Team in Co-Optima.

References

1. K. Maruta, T. Kataoka, N. Kim, S. Minaev, and R. Fursenko, "Characteristics of combustion in a narrow channel with a temperature gradient," *Proc. Combust. Inst.*, **30**:2429, 2005.
2. M. Hori, A. Yamamoto, H. Nakamura, T. Tezuka, S. Hasegawa, K. Maruta, "Study on octane number dependence of PRF/air weak flames at 1–5 atm in a micro flow reactor with a controlled temperature profile," *Combust. Flame*, **159**:959, 2012.

FY 2016 Publications/Presentations

1. M. McNenly et al., "Co-Optimization of Fuels and Engines (Co-Optima) – Simulation Toolkit Team," U.S. DOE Annual Merit Review and Peer Evaluation for the Vehicle Technologies Office, Project FT040, Washington, D.C., 2016.

IV. Co-Optimization of Fuels and Engines: Fuel Kinetics and Simulation

This section details the development and application of modeling capabilities to provide crucial insights into the fuel property impacts on engine performance. These physics-based models extend the range, confidence, and applicability of engine experiments and contribute to the fundamental understanding of combustion processes.

IV.1 Fuel Property Database

Overall Objectives

- Facilitate the successful co-optimization of fuels and advanced combustion engines, enabling the introduction of future fuel feedstocks and reducing the U.S. dependence on foreign oil
- Develop a fuel blending model based upon analytical approaches correlating molecular structure of fuel components to fuel properties and performance, generating a predictive tool for integration into a fuel properties database

Fiscal Year (FY) 2016 Objectives

- Conduct nuclear magnetic resonance (NMR) spectroscopic measurements needed to correlate Co-Optima fuel mixtures' chemical substructures, i.e., types of chemical bonds, with fuel properties
- Analyze fuels at high-pressures to observe phase change behavior under conditions simulating vehicle fuel injectors
- 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 2016 Accomplishments

- Developed strong chemical structure–property correlations for derived cetane number (DCN), T10, T50, and T90 based on one-dimensional NMR analyses of 24 gasoline boiling range fuels from bio-derived upgrading processes using regression modeling methods
- Explored property optimization methods, laying the groundwork for a fuel property blending model
- Tested diesel fuel surrogates and diesel fuels at pressures up to 380 MPa (~55 ksi) to assess fuel phase behavior at pressures reflecting 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 Projects: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling (AVFL-18a), Data Mining of FACE Diesel Fuels (AVFL-23), and Measuring Fuel Heat of Vaporization (AVFL-27)

**Tim Bays (Primary Contact),
John C. Linehan, John R. Cort,
Kristin H. Jarman, Gregory W. Coffey,
Alejandro Heredia-Langner,
Ahmet K. Bingol, and
Margaret C. Jones**

Pacific Northwest National Laboratory (PNNL)
PO Box 999
Richland, WA 99352
Phone: (509) 375-6900
Email: tim.bays@pnnl.gov

DOE Technology Development Manager:
Kevin Stork

Future Directions

- Refine structure–property correlations and develop additional correlations using available and new 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 and fuel components, to broaden the applicability of fuel structure–property correlations
- Continue to examine the high-pressure phase behavior of complex fuels and fuel blends to ascertain the structural origins of high-pressure phase behavior
- Continue collaborative work with members of the CRC's FACE Working Group and the Alternative and Surrogate Fuels projects ■

Introduction

Future fuels, produced by upgrading non-petroleum and/or petroleum-based feedstocks, can exhibit significant variability in composition and chemical properties depending on the feedstock(s) and processing method(s) employed. A better understanding of the variability will allow the prediction of fuel properties, enabling better design of fuel system and engine components, thereby improving the performance of these fuels in advanced combustion engines. This project contributes to a task under the Co-Optimization of Fuels & Engines program

(Co-Optima), where the primary objective of Co-Optima is a 30% reduction in per-vehicle petroleum consumption beyond the 2030 gains achieved through business-as-usual evolutionary, regulatory-driven improvements. This program objective will be achieved through simultaneous development of engines and fuels. PNNL's specific objectives support the overall Co-Optima program by developing an understanding of the chemical structures contained within a fuel and linking those structures to fuel performance and physical properties. This understanding will be used to develop and inform a fuel blending model that uses the knowledge of the chemical structures within each fuel component, and proposes blending quantities of each component to meet a targeted set of fuel physical and performance specifications.

PNNL in collaboration with several national laboratories and industry partners, as well as CanmetENERGY, analyzed fuels from unconventional sources, such as oil sands, shale oils, renewable-derived fuels, and various distillate streams. PNNL has contributed to the characterization of the CRC FACE, as well as other fuel sets from the CRC. PNNL has worked to 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. These and other correlations were developed and will be expanded under the DOE Co-Optima program. With a greater knowledge of fuel structures and their resulting chemistries, fuel and engine companies can cooperate to design robust fuels, resolving potential incompatibilities with existing and next generation engines. In addition, fuel additive companies can investigate operability requirements, such as cold flow properties, and the effectiveness and compatibility of current additives with these new fuels. Achieving optimum performance in future advanced combustion engines will hinge on the co-development of fuels and aftertreatment options, and require a comprehensive understanding of the impacts of fuel chemistry on the vehicle as a system.

Approach

PNNL examined a variety of fuel 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. These samples were obtained through a variety of mechanisms, most notably leveraging fuel mixtures produced from projects funded by the Bioenergy Technologies Office, as well as through our collaborations with other national laboratories and with the CRC's Advanced Vehicle/Fuel/Lubricants (AVFL) Committee members. Analyses emphasized quantitative NMR measurements for the purpose of

linking specific molecular substructures to fuel physical and performance properties. The results of these analyses were then combined through regression-based modeling methods to tie fuel performance properties, such as lubricity, DCN, and properties inferred from a fuel distillation curve, to specific molecular substructures. Additional analytical capabilities under development include the use of two-dimensional NMR techniques, such as heteronuclear single quantum coherence and heteronuclear multiple bond correlation, and two-dimensional gas chromatography. To gain full benefit from these analysis tools it will be necessary to: (1) incorporate all analytical data sets into one format (fuel property database) 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

This study probes the questions of whether NMR features representing certain molecular substructures in the fuel correlate with the available fuel properties and whether those features are good predictors of those fuel properties. Fuel property trends, such as increasing cetane number with increasing chain length or increasing octane number with increased branching, are readily observed for pure chemicals. Trends from secondary structural effects, such as the length and relative position of chain branching, require testing of more complex, pure chemicals. Understanding the interaction of these trends is important for assessing the properties of mixtures where the identity and quantity of each constituent are known. An understanding of complex fuel blends, where the identities of hundreds or thousands of individual chemicals are not known, can be obtained by examining NMR spectra. Using NMR spectra, chemical contributions for each molecular substructure, e.g., proton or carbon type, or functional group, can be considered quantitatively through regression modeling, yielding an understanding of the relative importance of each substructure. In this study PNNL collected ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data and conducted a comprehensive statistical analysis of 24 bio-derived chemical mixtures fractionated into gasoline and diesel boiling ranges. The majority of the samples were in the gasoline boiling range to align with Co-Optima program

goals. Samples resulted from previous work conducted at PNNL under Bioenergy Technologies Office funding, and generally were derived from either pyrolysis or hydrothermal liquefaction processes, with some form of upgrading and separation to remove undesirable components. Five of the fuel samples contained oxygenates, while the remaining 19 samples either did not contain appreciable oxygenates, or the quantities were below NMR detection thresholds of about 0.1% of protons or carbons associated with an oxygen-containing functional group. Fuel performance properties, such as DCN, were obtained using ASTM methods. Regression models were developed using ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data individually, and combined together, for DCN from ignition delay (ASTM 6890) and T10, T50, and T90 from simulated distillation (ASTM 2887). Combining the data from the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra improved each of these correlations. Strong correlations between highly substituted aromatics, diaromatics, and cycloparaffins were observed. Specific spectral regions of correlation include CH in naphthalenes and CH_3 -substituted aromatics in both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. These correlations are not surprising since cyclic structures, like aromatic or cycloalkane rings, along with the number, location, and length of attached carbon chains, influence the molecular weight of molecules within a fuel. When treated quantitatively, their influence on key points along the distillation curve (T10, T50, and T90) can be assessed. Similarly, these structures contribute to the formation and stabilization of radicals during combustion, impacting the propensity of a fuel to autoignite, as measured by DCN. A quantitative understanding of the relative populations of each of these chemical substructures is critical for assessing a fuel's physical and performance properties. As a specific example, preliminary results of the regression modeling for T90 using eight NMR integration regions incorporating the substructures mentioned above, three from ^1H NMR spectra and five from $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, are provided in Figure 1. In Figure 1, the measured T90 is shown on the X-axis, and the corresponding predicted T90 is shown on the Y-axis. Points plotted as red open circles represent the case where all available data values were used to develop the regression model, while points plotted as blue asterisks show solid validation results using a leave-one-out approach. In the leave-one-out approach, as each individual T90 value was removed from the dataset, a new model was built with the remaining data and then used to predict the T90 value for the fuel being left out. Good correlations between molecular structure data and the other properties examined were also obtained. Additional fuel data sets are expected to be incorporated into these correlations broadening the correlation beyond bio-derived fuel components. PNNL will continue to seek

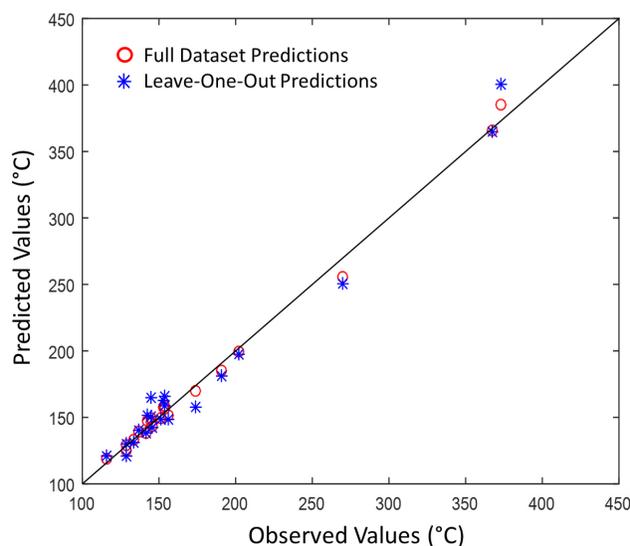


Figure 1. Predicted versus measured 90% volume recovered (T90) from a simulated distillation (ASTM D2887) of the fuel. Regression results for 24 bio-derived fuel mixtures predicting T90 are derived by examining ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral regions corresponding to molecular substructures of interest and selecting combinations of regions that result in a model having statistically significant terms and good predictive performance properties. In this preliminary model, T90 was found to correlate strongly to a combination of regions indicative of highly substituted aromatic, diaromatic, and cycloparaffins. Specific spectral regions of correlation include CH in naphthalenes and CH_3 -substituted aromatics in both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The observed T90 from ASTM 2887 is shown on the X-axis, and the corresponding predicted T90 is shown on the Y-axis. Points plotted as red open circles represent the case where all available data values were used to develop the regression model, while points plotted as blue asterisks show validation results using a leave-one-out approach.

correlation between chemical substructures and physical or performance properties in order to better predict the behavior of fuel components.

Extending work performed in FY 2015 [1], PNNL has continued to investigate the high-pressure phase behavior of fuels. This work combines the need to understand the effects of pressure on fuels having high concentrations of one or more “pure” chemical components, which is expected to be important when considering bio-derived fuel blends under Co-Optima, and the need to mitigate the pressure-induced fuel solidification observed in the CRC diesel fuel surrogates [1] as part of a CRC activity led by Dr. Charles Mueller of Sandia National Laboratories and Dr. William Cannella of Chevron [2,3]. As is the case for today's ethanolic gasoline, where a blendstock for oxygenate blending is combined with ethanol to

achieve the desired fuel properties, future fuels may be similarly formulated but instead of ethanol or in addition to ethanol, one or more “pure” chemicals could be added. The presence of such new chemicals could induce an unexpected phase change within the fuel under high pressures, potentially blocking the very narrow channels inside a fuel injector, restricting the flow of fuel to the engine, or changing the composition of the fuel. FY 2015 results showed that at least one component, the majority of which is the *n*-alkane, in each of four surrogate diesel fuels solidifies at or above room temperature, as pressure increases. Temperatures well above room temperature are required to maintain a homogeneous solution [1]. Efforts to ameliorate the partial solidification of the surrogate diesel fuels are ongoing. Figure 2 shows representative solid–liquid equilibria lines for four materials: *n*-hexadecane, as a reference material; Diesel Surrogate V0b, a five-component diesel fuel surrogate [3] reported as Diesel Surrogate 2 in FY 2015; GTL1, a low aromatic and low cycloparaffin fuel; and ULSD1, an ultra-low sulfur diesel. Extensive descriptions of GTL1 and ULSD1 are reported elsewhere [4]. Each material can be expected

to remain a liquid at temperatures above its respective trendline (solid or dashed line) at a given pressure. Below its respective trendline, a pure material will solidify, and a multicomponent material will have at least one component freeze out. Equations are presented near each respective trendline in a color matching the trendline and data for the four materials studied. GTL1 and ULSD1 represent diverse diesel fuels, and a baseline from which to study methods for influencing the solid–liquid equilibria in real fuel and surrogate fuel samples. From the data shown, it would be highly desirable to lower the solid–liquid equilibrium line of Diesel Surrogate 2 by 20–30°C in order to ensure single-phase behavior throughout the fuel system. It is not known whether this partial fuel solidification affects the fuel performance in an engine, however, complete fuel solidification would block the narrow fuel injector channels. 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 where system temperatures and pressures are near the solid–liquid equilibrium line [3].

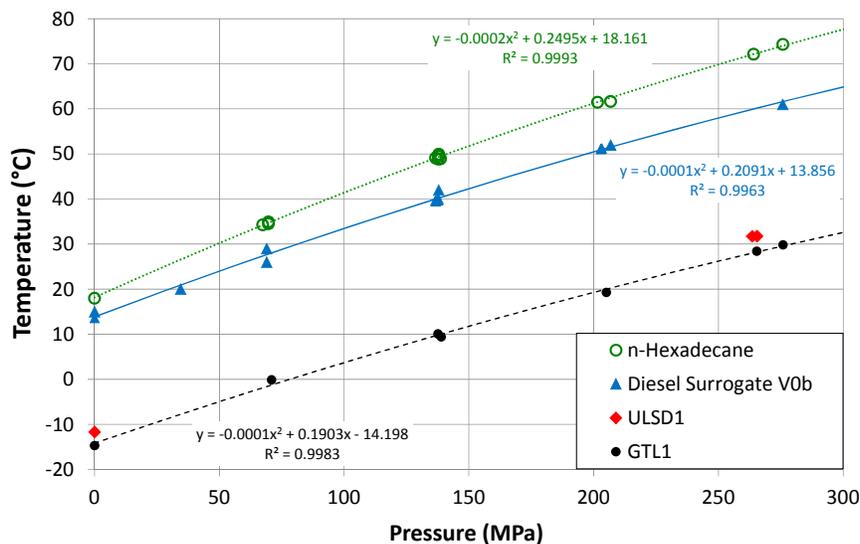


Figure 2. Comparison of the solid–liquid equilibria for *n*-hexadecane, a diesel fuel surrogate, and two diesel fuels. Data points for each material are shown as indicated, as well as the trendlines resulting from the data. *n*-hexadecane (green open circles) was used to validate the results obtained in the high-pressure system and compares favorably with data reported in the literature [5]. Diesel Surrogate V0b (blue triangles) is a diesel surrogate consisting of five pure chemical components [1–3]. ULSD1 (red diamonds) is a commercial ultra-low sulfur diesel [4] and GTL1 (black circles) is an advanced alternative fuel derived from a gas-to-liquids process [4]. Trendlines and equations representing the trendlines are presented for each material, where sufficient data was collected. Each material can be expected to remain a liquid at temperatures above its respective trendline at a given pressure. Below its respective trendline, a pure material will solidify and a multicomponent material will have at least one component freeze out.

Conclusions

- PNNL is developing a toolkit of NMR approaches 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.
- Understanding the high-pressure phase behavior of simple and complex surrogate and commercial fuel mixtures will ensure that unexpected phase changes are not encountered allowing fuel surrogates to be used by researchers without questioning the chemical integrity of the surrogate system, and new fuel components can be introduced without uncertainty about temperature, pressure, or concentration constraints on phase behavior.

FY 2016 Presentation

1. McCormick, R.L.; Fioroni, G.; Szybist, J.; Bays, T.; Miles, P.; McNeely, M.; Pitz, B.; Luecke, J.; Ratcliff, M.; Zigler, B.; Goldsborough, S. Co-Optimization of Fuels and Engines Fuel Property Team, Part 1 – Fuel Properties and Chemical Kinetics, U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, Vehicle Technologies Office Merit Review, Washington, D.C., June 9, 2016.

References

1. Stork, K. *Fuel and Lubricant Technologies, 2015 Annual Report*; U.S. Department of Energy, Energy Efficiency & Renewable Energy, Vehicle Technologies Office: <https://energy.gov/eere/vehicles/downloads/vehicle-technologies-office-fuel-and-lubricant-technologies-2015-annual>, April 2016, pp 114–119.
2. Mueller, C.J.; Cannella, W.J.; Bruno, T.J.; Bunting, B.; Dettman, H.D.; Franz, J.A.; Huber, M.L.; Natarajan, M.; Pitz, W.J.; Ratcliff, M.A.; Wright, K., Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics. *Energy & Fuels* **2012**, *26* (6), 3284–3303.
3. 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* **2016**, *30* (2), 1445–1461.
4. Cannella, W.; Fairbridge, C.; Gieleciak, R.; Arboleda, P.; Bays, T.; Dettman, H.; Foster, M.; Gunter, G.; Hager, D.; King, D.; Lay, C.; Lewis, S.; Luecke, J.; Sluder, S.; Zigler, B.; Natarajan, M. *Advanced Alternative and Renewable Diesel Fuels: Detailed Characterization of Physical and Chemical Properties*; CRC Report No. AVFL-19-2; Coordinating Research Council: Alpharetta, GA, 2013.
5. 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.

IV.2 Fuel Property Blend Model

Overall Objectives

LLNL will develop chemical models and associated correlations to predict the blending behavior of bio-derived fuels when mixed with conventional fuels like gasoline and diesel fuels.

Fiscal Year (FY) 2016 Objectives

LLNL will predict the blending behavior of fuel components and blends for octane number and octane sensitivity (OS).

FY 2016 Accomplishments

- Predicted Research Octane Number (RON) for a series of compounds in different chemical classes (e.g., n-alkanes, alkenes, aromatics, cycloalkanes, alcohols) and traced the chemical kinetic origin of OS
- Demonstrated the ability to compute RON for mixtures of ethanol with gasoline surrogates consisting of iso-octane, n-heptane (primary reference fuel [PRF]); and toluene, iso-octane, and n-heptane (toluene primary reference fuel)

Future Directions

- Predict octane blending behavior of two to three classes of advanced performance fuels with two to three core gasoline fuels
- Predict blend behavior for candidate advanced-performance fuels in core fuels at advanced spark ignition (SI) and advanced compression ignition (CI) engine conditions ■

Introduction

The combustion of transportation fuels in internal combustion engines is generally characterized by important properties such as RON, Motor Octane Number (MON), cetane number, and flame speed, but predicting these properties for fuels is challenging because of complex chemical–kinetic interactions of fuel components that cause non-linear behavior. To address this issue, the LLNL kinetic modeling team is developing chemical kinetic models that can predict RON, MON, and flame speed, and can model the complex behavior of these mixtures under conditions in advanced SI and CI engines. These accurate and validated chemical kinetic models are critical for developing insight into how fuel properties impact engine performance. To use these chemical kinetic

**William J. Pitz (Primary Contact),
Charles K. Westbrook, Marco Mehl,
Scott W. Wagnon, Kuiwen Zhang,
Goutham Kukkadapu**

Lawrence Livermore National Laboratory (LLNL)
PO Box 808, L-372
Livermore, CA 94551
Phone: (925) 422-7730
Email: pitz1@llnl.gov

DOE Technology Development Manager:
Kevin Stork

models in multidimensional simulation codes, the models are reduced in size and employed to simulate combustion in advanced SI and advanced CI engines. These insights and combustion simulations will guide efforts to discover promising bio-derived fuel and core fuel blends that provide the desired engine combustion properties under advanced SI and CI engine conditions.

Approach

Chemical kinetic models for bio-derived fuel components of interest for blending with gasoline and diesel fuels are developed. Next, these chemical kinetic models are combined with kinetic models for conventional fuels to represent next-generation ground transportation fuels. Correlations are developed between engine combustion properties (such as RON, MON, OS, and cetane number) and key quantities from the chemical kinetic model (such as ignition delay and slope of the ignition delay curve in the low temperature chemistry region). Using the detailed chemical model and these correlations, key engine combustion properties can be predicted. Also, the detailed chemical kinetic model can be used to interpret the results in terms of the importance of different chemical paths identified by the simulations.

Results

In order to simulate the behavior of different fuel components and gasoline core fuels, a chemical kinetic model with fuel molecules from five chemical classes was assembled. The chemical classes consisted of n-alkanes, alkenes, alkyl-benzenes, cycloalkanes and alcohols, and they contained a total of ~35 different fuel molecules

[1]. The chemical kinetic model was used to simulate the RON behavior of fuel components in each of the above chemical classes. In order to compute RON, a methodology for simulating RON and MON developed at Sandia National Laboratories was followed (see Figure 2 in report II.1, “Alternative Fuels DISI Engine Research – Autoignition Metrics,” by Magnus Sjöberg). Two pressure histories from the direct injection SI engine at Sandia National Laboratories were identified that are representative of RON and MON pressure histories. The pressure histories included the effect of flame propagation and piston motion, but only a very small effect of heat release due to end-gas autoignition reactions since a high RON E30 fuel was used. In the RON simulations reported here, the RON-like pressure history was followed for each of the fuel components in the different chemical classes in order to compute their autoignition behavior under RON conditions. Each of the component fuels autoignited and their ignition time was noted. The ignition behavior of fuel components in the different chemical classes is shown in Figure 1. Also shown in Figure 1 are the ignition times using the RON-like pressure history for PRF mixtures that define the octane scale. Using this scale, the RON values of the fuel components for the different chemical classes can be approximately determined from their computed ignition delay time. (The scatter around the PRF calibration line is due to uncertainties in the use of the single pressure curve to represent RON behavior, uncertainties in kinetic rate constants used in the simulations, and uncertainties

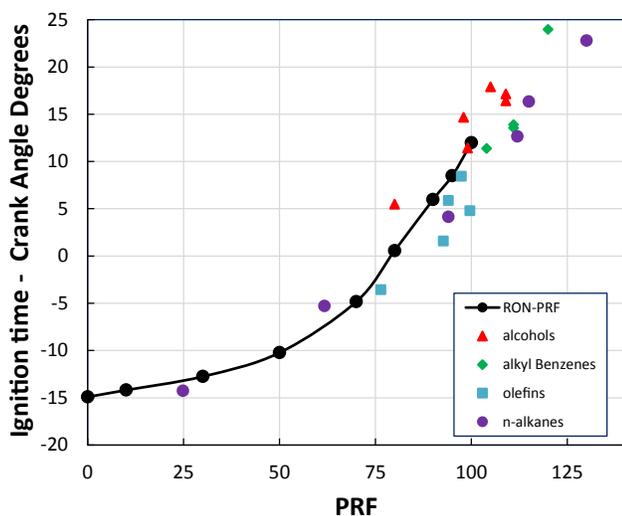


Figure 1. Computed autoignition times for fuels in different classes. Calibration points from PRF fuel mixtures are shown as the solid line and black points. The solid line defines the correlation between computed ignition delay and RON. To predict the RON of a neat component, its ignition delay was computed and the correlation was applied.

in the original RON measurements.) These simulations demonstrate a capability to compute RON for a variety of fuel components from different chemical classes.

The behavior of the fuel components in each chemical class was examined with an emphasis on comparing the behavior of fuels with different measured OSs. OS is the difference between RON and MON and is an important property that enables advanced SI engine operation. First, olefin and n-alkane behavior were examined and compared. It was found that when olefins were subjected to the RON-like pressure history, they exhibited only small amounts of low temperature reactivity and heat release compared to n-alkanes. These olefins produced resonantly stabilized radicals that suppressed low temperature chemistry. They also had high OS compared to n-alkanes which have near-zero OS. Another chemical group that exhibits high OS is the alcohol chemical class. This class also exhibited only small amounts of low temperature activity compared n-alkanes. The lack of low temperature reactivity was also traced the production of unreactive radicals in alcohols, as was seen in the olefin class. The source of the nonreactive radicals was due to the presence of an alpha hydrogen next to the OH group in alcohols that is easily extracted. The radical formed acts similarly to the resonantly stabilized radicals from olefins. Finally, the alkyl-aromatics chemical class was examined, and it was concluded that this class also forms resonantly stabilized radicals (benzylic radicals) and behaves similarly to the olefin chemical class. After examining the five chemical classes, it was concluded that the presence of OS was due to the tendency of a fuel to form resonantly stabilized radicals (or other similarly unreactive radicals) that fail to produce significant low temperature chemistry. To illustrate this behavior, Figure 2 shows four fuels with the same carbon skeletal structure that have much different OSs. N-hexane is an n-alkane that shows a significant low temperature heat release peak that indicates the presence

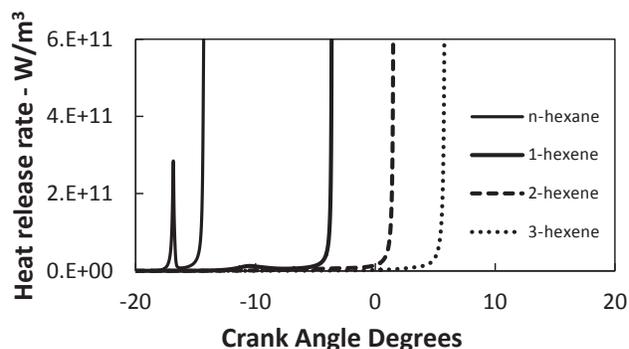


Figure 2. Computed rates of heat release for n-hexane and three hexene isomers using a using a RON-like pressure history

of substantial low temperature reactivity and it has zero OS (based on the definition of the octane scale). On the other hand, hexene isomers (Figure 2) show negligible low temperature heat release peak indicating the absence of low temperature reactivity and the possession of high OS. In summary, the origin of high OS was traced to the absence of low temperature chemistry paths due to a variety of chemical causes, with the formation of resonantly stabilized fuel radicals being a primary cause. Other causes included the lack of sufficient carbon-chain length to allow low temperature chemistry reactions to occur and the presence of molecular structures that allow limited low temperature reactivity, like the five-membered ring in the cyclopentane [2].

It is important to predict the behavior of bio-derived fuels when blended in gasoline fuels to identify the fuels with the most attractive properties for advanced SI engine applications. In order to achieve this goal, the LLNL kinetics team has predicted the RON and OS behavior of blends. To predict these metrics, quantities predicted by the model (ignition delay and slope in the negative temperature coefficient region) were correlated to anti-knock index (AKI) and OS. One correlation predicts the AKI from the ignition delay at 825 K and 25 atm, and the other correlation predicts the OS from the slope in the negative temperature coefficient region [3]. Since AKI is $(RON + MON)/2$, RON was determined by adding the AKI prediction with half of the OS prediction. Figure 3 shows the predicted and measured blending behavior for RON when ethanol is blended into different gasoline PRF mixtures. As seen in the figure, the experimentally measured RON behavior [4] of these blends is well predicted by the model using the LLNL correlations.

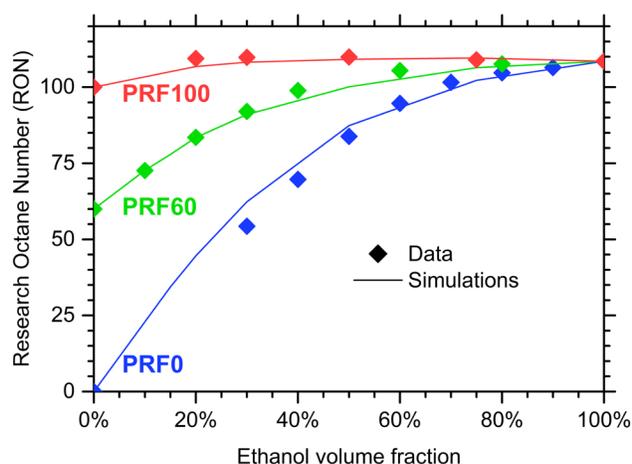


Figure 3. The experimentally measured [4] and predicted RON for ethanol blended into three PRF mixtures. PRFxx are primary reference fuels of xx% iso-octane in n-heptane

Conclusions

- A newly developed gasoline surrogate chemical kinetic model with many added fuel components was used to predict RON for five chemical classes and 35 compounds.
- The above chemical kinetic model was also used to explain the origin of OS which was generally traced to the presence of unreactive fuel radicals.
- Using correlations developed at LLNL, a capability was demonstrated to predict RON of different gasoline PRFs blended with various amounts of ethanol.

Acknowledgements

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

1. C.K. Westbrook, M. Mehl, W.J. Pitz and M. Sjöberg, "Chemical kinetics of octane sensitivity in a spark-ignition engine," *Combust. Flame* (175) (2017) 2–15.
2. M.J. Al Rashidi, S. Thion, C. Togbé, G. Dayma, M. Mehl, P. Dagaut, W.J. Pitz, J. Zádor and S.M. Sarathy, "Elucidating reactivity regimes in cyclopentane oxidation: Jet stirred reactor experiments, computational chemistry, and kinetic modeling," *Proc. Combust. Inst.* (2017).
3. M. Mehl, J.Y. Chen, W.J. Pitz, S.M. Sarathy and C.K. Westbrook, "An Approach for Formulating Surrogates for Gasoline with Application toward a Reduced Surrogate Mechanism for CFD Engine Modeling," *Energy & Fuels* 25 (11) (2011) 5215–5223.
4. T.M. Foong, K.J. Morganti, M.J. Brear, G. da Silva, Y. Yang and F.L. Dryer, "The octane numbers of ethanol blended with gasoline and its surrogates," *Fuel* 115 (2013) 727–739.

FY 2016 Publications/ Presentations

1. C.K. Westbrook, M. Mehl, W.J. Pitz and M. Sjöberg, "Chemical kinetics of octane sensitivity in a spark-ignition engine," *Combust. Flame* (175) (2017) 2–15.
2. C.-W. Zhou, J.M. Simmie, W.J. Pitz and H.J. Curran, "Towards the Development of a Fundamentally-based Chemical Model for Cyclopentanone: High Pressure Limit Rate Constants for H-atom Abstraction and Fuel Radical Decomposition," *J. Phys. Chem. A* (2016).

3. M.J. Al Rashidi, S. Thion, C. Togbé, G. Dayma, M. Mehl, P. Dagaut, W. J. Pitz, J. Zádor and S.M. Sarathy, “Elucidating reactivity regimes in cyclopentane oxidation: Jet stirred reactor experiments, computational chemistry, and kinetic modeling,” Proc. Combust. Inst. (2017).

IV.3 Kinetic Mechanism Development

Overall Objectives

- Develop chemical kinetic models for bio-derived blendstocks and base fuels (e.g., gasoline and diesel) to determine their behavior at advanced spark ignition and advanced compression ignition conditions for Co-Optima
- Use chemical kinetic models to simulate combustion properties under relevant engine conditions

Fiscal Year (FY) 2016 Objectives

- Develop a gasoline surrogate model for E10 (10% ethanol, 90% gasoline blend) RD5-87 used in Sandia National Laboratories homogeneous charge compression ignition engine experiments
- Develop a preliminary chemical kinetic model for anisole, a model component to represent biomass pyrolysis fuel and a bio-derived compound for advanced spark ignition
- Develop validated and improved gasoline surrogate model mechanism for Coordinating Research Council (CRC) Fuels for Advanced Combustion Engines (FACE) Fuel F with ethanol up to 30%, using rapid compression machine (RCM) experiments from Argonne National Laboratory (ANL)

FY 2016 Accomplishments

- Developed chemical kinetic surrogate model for the three Co-Optima core fuels to be used for fuel property hypothesis studies
- Developed a gasoline surrogate mixture model for E10 RD5-87 gasoline
- Developed a preliminary chemical kinetic model for anisole
- Validated a gasoline surrogate mechanism with ethanol by comparing simulated ignition delay times with measured ignition delay times in the ANL RCM for CRC FACE F with varying amount of ethanol

Future Directions

- Develop chemical kinetic models for bio-derived blendstocks relevant to advanced compression ignition engine conditions

**William J. Pitz (Primary Contact),
Marco Mehl, Scott W. Wagnon,
Kuiwen Zhang, Goutham Kukkadapu,
Charles K. Westbrook**

Lawrence Livermore National Laboratory (LLNL)
PO Box 808, L-372
Livermore, CA 94551
Phone: (925) 422-7730
Email: pitz1@llnl.gov

DOE Technology Development Manager:
Kevin Stork

- Predict blending behavior of down-selected bio-blend stocks with Co-Optima core fuels under relevant engine conditions ■

Introduction

Predictive chemical kinetic models are needed to represent bio-derived blendstocks downselected by Co-Optima and their mixtures with conventional fuels like gasoline and diesel. These kinetic models can be used in computational fluid dynamics simulations of advanced spark ignition and advanced compression ignition engines so that the behavior of these fuel blends can be predicted in these engines. Enabled by kinetic models, computational fluid dynamics simulations can be used to optimize fuel formulations for advanced combustion engines so that the engine efficiency and fossil fuel displacement goals, and minimum harmful emissions can be achieved.

Approach

To develop chemical kinetic models for blends of bio-derived fuels and conventional transportation fuels, chemical kinetic models for each bio-derived fuel of interest are developed, as needed. These fuel component models are developed by identifying the reaction paths for the bio-derived fuel and assembling the associated rate constants, thermodynamic, and transport data. Next, these models for bio-derived fuels are combined with chemical kinetic surrogate models for conventional fuels to represent blends of bio-derived fuels and conventional transportation fuels. The mechanisms are validated by comparison of computed results to

fundamental experimental data from RCMs, shock tubes, and laboratory flames. Then the mechanisms are used in multidimensional engine simulation codes for simulating combustion 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 harmful emissions.

Results

Anisole is a bio-derived fuel that was among those fuels considered by Co-Optima for advanced spark ignition engine applications. Among its features, anisole has attractive combustion properties for gasoline modes of operation including a high blending Research Octane Number (120 at 10% volume anisole) and low blending Motored Octane Number (98 at 10% volume anisole) [1]. Production pathways have been identified for anisole, including pyrolysis from biomass. In FY 2016, an anisole chemical kinetic model was developed. Using the new

chemical kinetic model, computed species concentrations were compared to literature data of measured species concentrations in a jet-stirred reactor (JSR) at pyrolysis and oxidative conditions [2]. A comparison of the model (lines) and the experiment (symbols) for stoichiometric fuel/O₂/N₂ mixtures at 1 atm is shown in Figure 1 and the agreement is good. Additional comparisons have been made with new experimental data from the JSR obtained by Dr. Dayma, CNRS, Orleans, France. Also, flame speeds have been computed using the chemical kinetic model and compared to experimental data obtained from Dr. Nilsson at Lund University (Figure 2). Both the computations and the measurements show that anisole exhibits a higher flame speed compared to conventional gasoline components like n-heptane. Although the predicted flame speed was 10% higher than the measured flame speed, such agreement is typical of that found in the literature and is acceptable. The new mechanism will allow the simulation of anisole when blended with gasoline under advanced spark ignition engine conditions.

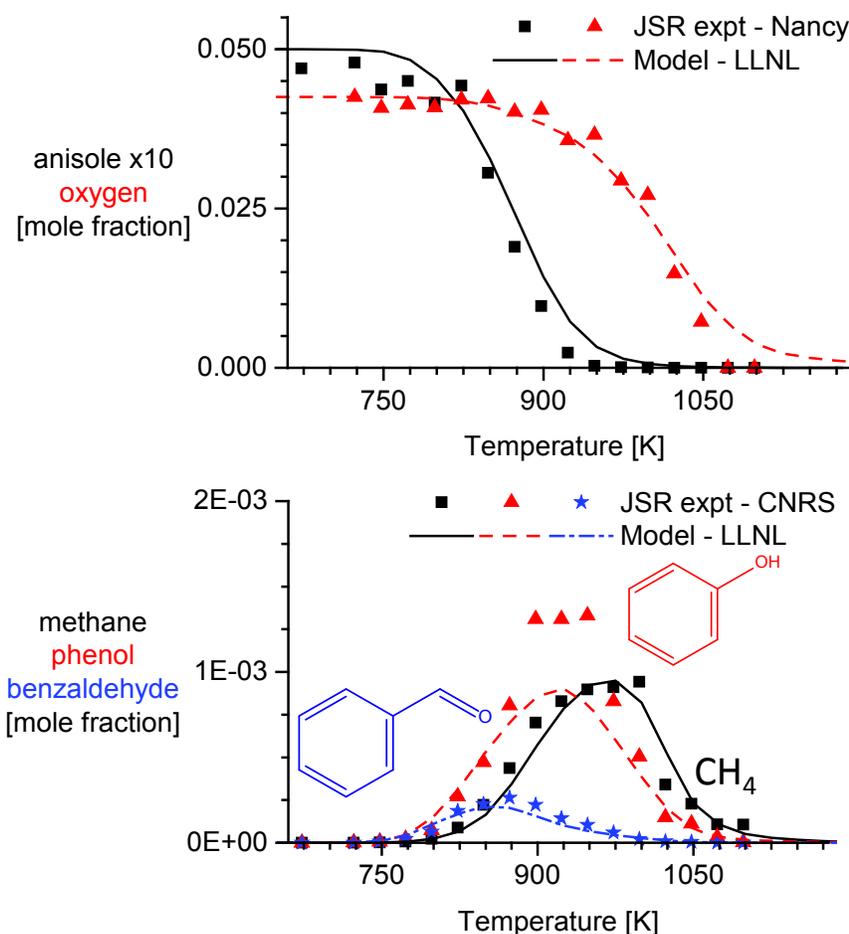


Figure 1. Comparison of simulated and measured species mole fractions in a JSR for anisole/O₂/N₂ stoichiometric mixtures at 1 atm [2]

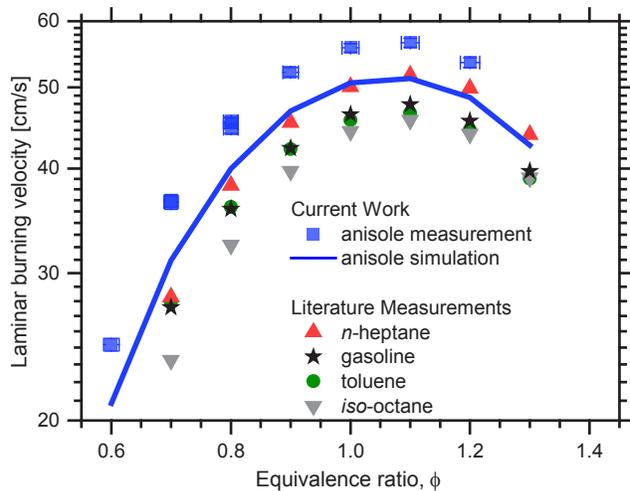


Figure 2. Comparisons of simulated (LLNL) and measured flame speeds (Lund University) and comparisons to flame speeds of gasoline and other representative gasoline components [4]

Ethanol is a commonly used bio-derived fuel blendstock in market gasolines in the United States and has high octane, high sensitivity properties that make it attractive for advanced spark ignition engines. During FY 2016, the LLNL gasoline surrogate model with ethanol was tested against experimental data from the ANL's RCM for a gasoline containing ethanol. This gasoline was blended by adding varying amounts of ethanol to a gasoline reference fuel (CRC FACE F [3]) which has a high Research Octane Number and a high octane sensitivity. Ignition delay times were measured in the RCM covering a wide range of temperatures and pressures of 21 and 40 bar. A comparison of the computed ignition delay times with the measured ignition delay times is shown in Figure 3 and the agreement is reasonable. Additional RCM and engine experiments are planned for RD5-87 which is a fully blended gasoline reference fuel with 10% ethanol that is intended to match the properties of an average market gasoline and has an anti-knock index (AKI) of 87. In FY 2016, a gasoline surrogate mixture was developed to match the AKI, octane sensitivity, chemical classes, and C/H ratio of RD5-87. A comparison of chemical classes in the surrogate fuel and the target RD5-87 gasoline is shown in Figure 4 with very good matching of the classes.

In FY 2016, Co-Optima developed core fuels to evaluate the effect of fuel composition on advanced spark ignition engine performance. Three core fuels were developed which all have a high Research Octane Number value of 98: an alkylate fuel, an aromatic fuel, and a fuel with ethanol. In FY 2016, surrogate mixture kinetic models were developed by the LLNL kinetics modeling team

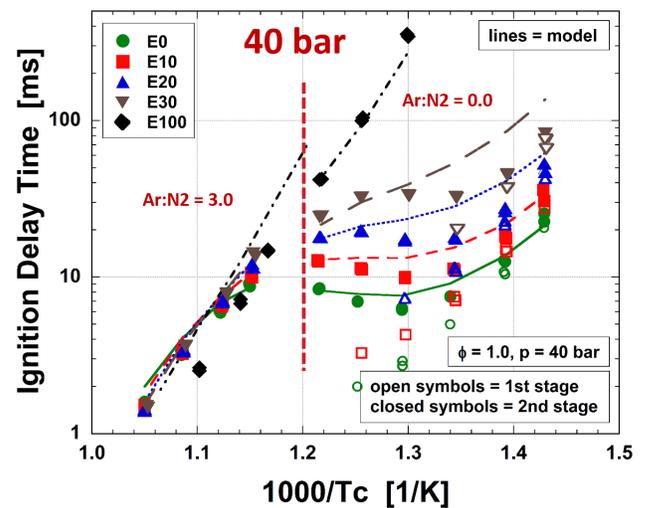


Figure 3. Measured (RCM) and simulated ignition delay times of gasoline CRC FACE Fuel F with 0%, 10%, 30%, and 100% ethanol. RCM experiments were performed at ANL in Scott Goldsborough's lab.

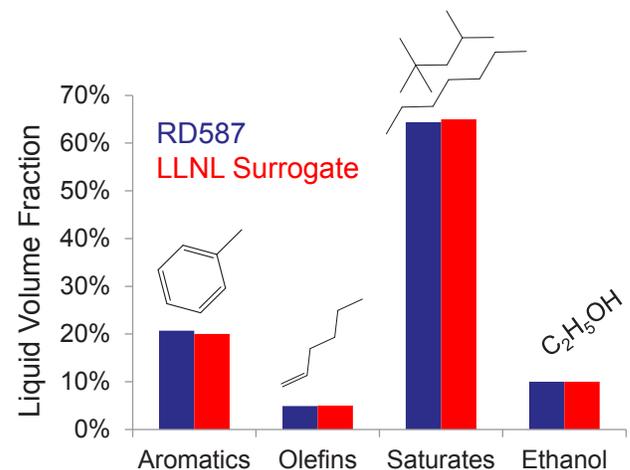


Figure 4. Matching of the chemical classes measured in RD5-87 and represented by the LLNL surrogate mixture composition

to represent each of these core fuels. The AKI, octane sensitivity, chemical class distribution, and distillation curve of each of the Co-Optima base fuels were matched by surrogate mixtures comprised of four, seven, and eight components for the alkylate, aromatic, and ethanol base fuels, respectively. The matching of the experimentally measured distillation curve using five- and seven-component fuel surrogates for the aromatic core fuel is shown in Figure 5. The agreement between the experimental distillation curve of the aromatic core fuel and the distillation curve predicted for the seven-component surrogate mixture is good.

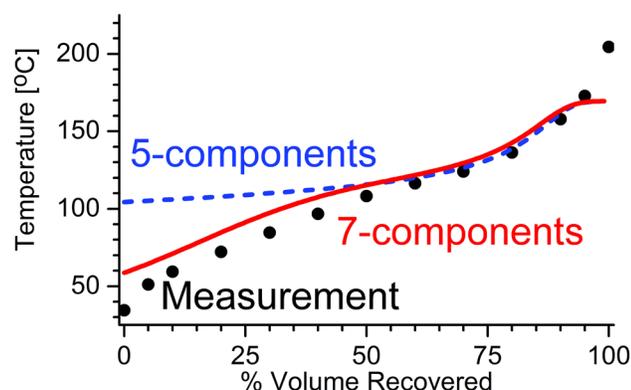


Figure 5. Simulated (curves) and measured (points) distillation curve behavior. A five- and seven-component surrogate fuel mixture was tested for Co-Optima aromatic core fuel.

Conclusions

- A preliminary chemical kinetic model for anisole, a bio-derived fuel with attractive properties for advanced spark ignition engines, was developed.
- The chemical kinetic models to represent gasoline fuels with ethanol was further validated using experimental data from ANL's RCM.
- Chemical kinetic surrogate models to represent Co-Optima core gasoline fuels were developed.

Acknowledgements

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

1. R.L. McCormick, M.A. Ratcliff, E. Christensen, L. Fouts, J. Luecke, G.M. Chupka, J. Yanowitz, M. Tian and M. Boot, "Properties of Oxygenates Found in Upgraded Biomass Pyrolysis Oil as Components of Spark and Compression Ignition Engine Fuels," *Energy & Fuels* 29 (2015) 2453–2461.
2. M. Nowakowska, O. Herbinet, A. Dufour and P.-A. Glaude, "Detailed kinetic study of anisole pyrolysis and oxidation to understand tar formation during biomass combustion and gasification," *Combust. Flame* 161 (6) (2014) 1474–1488.

3. FACE, "CRC Fuels for Advanced Combustion Engines Working Group (FACE)," <http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/FACE/index.html>, 2014.
4. L. Sileghem, V.A. Alekseev, J. Vancoillie, K.M. Van Geem, E.J.K. Nilsson, S. Verhelst and A.A. Konnov, "Laminar burning velocity of gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene," 112 (2013) 355–365.

FY 2016 Publications/ Presentations

1. Westbrook, C.K., Mehl, M., Pitz, W.J. and Sjöberg, M., "Chemical Kinetics of Octane Sensitivity in a Spark-Ignition Engine," *Combustion and Flame* 175 (2017) 2–15.
2. C.-W. Zhou, J.M. Simmie, W.J. Pitz and H.J. Curran, "Towards the Development of a Fundamentally-based Chemical Model for Cyclopentanone: High Pressure Limit Rate Constants for H-atom Abstraction and Fuel Radical Decomposition," *J. Phys. Chem. A* (2016).
3. M.J. Al Rashidi, S. Thion, C. Togbé, G. Dayma, M. Mehl, P. Dagaut, W.J. Pitz, J. Zádor and S.M. Sarathy, "Elucidating reactivity regimes in cyclopentane oxidation: jet stirred reactor experiments, computational chemistry, and kinetic modeling," *Proc. Combust. Inst.* (2017).
4. 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* 30 (2) (2016).

IV.4 Kinetic Mechanism Development and Validation

Overall Objectives

ANL will acquire autoignition data for a variety of real and surrogate petroleum-based and bioderived fuels using Argonne's Rapid Compression Machine (RCM) facilities, at conditions relevant to boosted spark-ignition (SI) and advanced compression ignition (ACI) engines, necessary for the development and validation of detailed and reduced chemical kinetic models.

Fiscal Year (FY) 2016 Objectives

ANL will acquire new data for primary reference fuel (PRF) blends covering a range of thermodynamic and fuel loading conditions relevant to boosted SI engines and collaborate with other fuel property team members to validate the performance of an updated detailed chemical kinetic model for gasoline.

FY 2016 Accomplishments

ANL acquired new data for PRF blends and interacted with the Lawrence Livermore National Laboratory (LLNL) fuel properties team members to validate and improve the performance of the LLNL gasoline surrogate model.

Future Directions

ANL will undertake measurements with other gasoline surrogate blends, future fuel candidates, and blends of these with surrogate mixtures and full boiling range fuels, so that synergistic and antagonistic behaviors can be quantified and better understood ■

Introduction

Fuel performance in modern spark ignition (SI) and advanced compression ignition (ACI) engines depends on many factors. Although autoignition chemistry is a primary driver, heat of vaporization and flame speed as well as chemical kinetic sensitivities to thermal and compositional stratification, are also important. Furthermore, the development and propagation/amplification of pressure waves after localized autoignition events leading to structural damage can also be dependent on the properties of the fuel. The capability to model and thus predict fuel performance based on fundamental measurements could significantly reduce the costs and time associated with co-optimizing fuels and engines.

The efforts of this project are primarily focused on acquiring experimental autoignition data that will:

S. Scott Goldsborough

Argonne National Laboratory (ANL)
9700 S. Cass Avenue
Bldg. 362
Argonne, IL 60439
Phone: (630) 252-9375
Email: scott.goldsborough@anl.gov

DOE Technology Development Manager:
Kevin Stork

(1) support the development, validation, and improvement of robust chemical kinetic mechanisms for real and surrogate fuels; and (2) provide insight into the chemical effects of fuel performance in boosted SI and ACI combustion engines.

Approach

The work pursued for this project seeks to address challenges associated with measuring the autoignition properties of potential future fuels and fuel blends, interpreting their performance in combustion engines (in terms of knock and combustion phasing), and properly modeling their behavior in zero- and multi-dimensional simulation frameworks. The approach used in this project is based on Argonne National Laboratory's Rapid Compression Machine facility, where this device is able to access experimental conditions that are directly relevant to modern SI and ACI engines, e.g., $T = 650\text{--}1,100\text{ K}$, $P = 10\text{--}100\text{ bar}$, $O_2 = 10\text{--}21\%$, and $\phi = 0.2\text{--}3.0$. Argonne National Laboratory's RCM typically uses 5–20 mL of fuel to conduct tests over a wide range of conditions with the autoignition chemistry studied over the low-temperature, negative temperature coefficient, and intermediate-temperature regimes.

RCMs have been used for nearly 100 years to investigate autoignition phenomena at engine-relevant conditions [1,2]. They are capable of creating and maintaining well-controlled, elevated temperature and pressure environments 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, and thermal/compositional stratification. Furthermore, the operating conditions, e.g., T , P , ϕ and O_2 , can be independently varied unlike in

internal combustion engines and this provides necessary insight. The ability to utilize wide ranges of fuel and oxygen concentrations within RCMs from ultra-lean to over-rich and spanning dilute to undiluted regimes offers specific advantages relative to other laboratory apparatuses such as shock tubes and flow reactors, where complications can arise under such conditions. Argonne's twin-piston RCM is utilized in this project where ignition delay times and heat release rates are measured.

Results

Autoignition measurements were conducted in FY 2016 with the intent to provide validation data for recent improvements in the LLNL gasoline surrogate model [3], which include the integration of an updated foundational chemistry model (ARAMCO Mech 2.0 [4]), as well as the implementation of new rate rules for low-temperature reactions covering normal (linear) alkane decomposition [5]. These new data are important for verifying the performance of the alkane component of the gasoline model, particularly since paraffins represent the primary component class of most all market gasolines (~50–75% vol/vol basis), and are often the largest surrogate class in gasoline surrogate blends.

Detailed experiments were conducted for PRF90 and PRF100 blends, where small increments in both temperature and pressure were used. This facilitated the resolution of both temperature and pressure dependencies on the autoignition process. Ignition delay times for first-stage and main ignition were quantified along with extents of low-temperature heat release. Low-temperature heat release has been observed to be important in both boosted SI and ACI engine regimes, so it is advantageous to use this as an additional target, or metric for the performance of the model.

Figure 1 illustrates a comparison of experimental measurements with the gasoline model predictions for the main ignition delay times, where this is presented as a function of inverse temperature. Here stoichiometric PRF90 mixtures diluted to near 6% by mass, i.e., 18.5% O₂ (by mole), where this is representative of the dilution typically found in the Research Octane Number test protocol, and in SI engines. Overall, the mechanism compares quite well with these recent results where trends in both temperature and pressure are fairly close to the experimental data. Some discrepancies are apparent however, where it is noticeable that the overall ignition delays are longer in the model at all of the pressures investigated.

Work in FY 2017 will coordinate with both LLNL as well as the National Renewable Energy Laboratory to

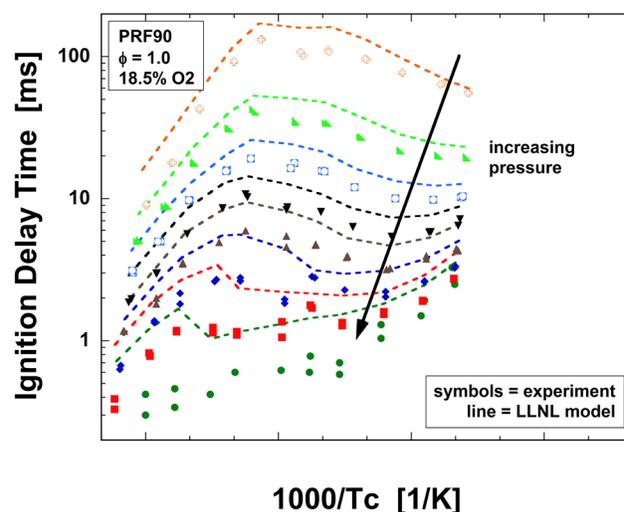


Figure 1. Comparison of experimental measurements and chemical kinetic predictions of autoignition delay time as a function of inverse temperature for stoichiometric PRF90 mixtures

provide complementary datasets and identify model sub-mechanisms, such as non-linear blending behavior, that can be improved through targeted tests. Measurements will be undertaken with other gasoline surrogate blends, future bioderived fuel candidates, and blends of these with surrogate mixtures and full boiling range fuels so that synergistic and antagonistic behaviors can be quantified and better understood. These are important towards properly representing blending octane behavior.

Conclusions

- New data have been acquired for a variety of PRF blends covering a wide range of thermodynamic conditions that are relevant to autoignition and knock in boosted SI engines.
- Comparisons are made against the updated LLNL gasoline surrogate model where fairly good performance is noted, though the model seems to be less reactive than the experiments over all of the conditions investigated.

References

1. C.-J. Sung and H.J. Curran, "Using rapid compression machines for chemical kinetics studies," *Prog. Energy Comb. Sci.* (44) 1–18, 2014.
2. S.S. Goldsborough, D. Longman, M.S. Wooldridge, R.S. Tranter and S. Pratt, "1st International RCM Workshop Meeting Report," August 28–29, 2012.

3. M. Mehl, J.Y. Chen, W.J. Pitz, S.M. Sarathy and C.K. Westbrook, "An approach for formulating surrogates for gasoline with application toward a reduced surrogate mechanism for CFD engine modeling," *Energy Fuels* 25 (2011) 5215–5223.
4. <http://www.nuigalway.ie/c3/aramco2>
5. L. Cai, H. Pitsch, S.Y. Mohamed, V. Raman, J. Bugler, H. Curran and S.M. Sarathy, "Optimized reaction mechanism rate rules for ignition of normal alkanes," *Combust. Flame* 173 (2016) 468–482.

IV.5 Ignition Kinetics Experiments and Simulations to Support Advanced Engine Development

Overall Objectives

- Develop experimental and simulation tools to characterize fuel ignition behavior in support of advanced combustion engine development, both spark ignition (SI) and compression ignition (CI)
- 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
- Develop understanding of fuel chemical and physical properties that enable furtherance of the DOE Co-Optima program research and development program for co-optimization of high performance fuels and high efficiency engines

Fiscal Year (FY) 2016 Objectives

- Assist in development and validation of chemical kinetic mechanisms for blends through ignition delay (ID) experiments and simulations
- Combine bench-scale, constant volume combustion chamber (CVCC) fuel autoignition studies with engine experiments to more extensively quantify fuel blend ignition performance than is presently possible with Research Octane Number (RON) and Motor Octane Number (MON)

FY 2016 Accomplishments

- Experimentally mapped and simulated parametric ignition delay data for various blends of iso-octane/ethanol, providing critical data to evaluate linking of kinetic mechanisms for blends
- Demonstrated the non-linear behavior of ethanol blends into iso-octane for low temperature heat release (LTHR) and the negative temperature coefficient (NTC) region
- Developed and validated a multizone modeling strategy for Ignition Quality Tester (IQT) simulations to evaluate kinetic mechanisms against experimental data
- Disseminated research with journal publications in *Fuel* and *Energy & Fuels*
- Commissioned and completed initial characterization of a flexible new Advanced Fuel Ignition Delay Analyzer

Bradley T. Zigler (Primary Contact), Jon Luecke, Matthew A. Ratcliff, and Gregory E. Bogin, Jr.

National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-4267
Email: brad.zigler@nrel.gov

DOE Technology Development Manager:
Kevin Stork

Subcontractor:
Colorado School of Mines, Golden, CO

(AFIDA), an NREL internally funded equipment purchase, to expand beyond IQT-based ignition kinetics studies

Future Directions

- Increase small volume ID screening evaluations of candidate compounds under Co-Optima
- Expand parametric ignition kinetics studies to blends with down-selected candidate compounds under Co-Optima, using the methodology established with ethanol baseline studies, enabling faster kinetic mechanism development and validation
- Perform modified Livengood–Wu knock integral calculations with IQT and AFIDA data in simulations of engine cycle data at knock limited conditions, establishing links between bench scale ID studies and single-cylinder engine studies [1]
- Correlate parametric ID studies with fuel composition for full boiling range gasoline research fuel blends, enabling subsequent correlation providing information beyond RON and sensitivity (S) to broader SI boosted engine performance studies ■

Introduction

A critical enabler to co-developing new, high performance fuel chemistries and highly efficient internal combustion engines is the ability to employ numerical simulation of

combustion strategy and chamber design. These numerical simulations rely on accurate computational fluid dynamics (CFD) linked with chemical kinetic mechanisms to predict ignition and combustion performance. Since fuel composition is complex, chemical mechanisms are based on surrogate compounds, frequently in representative blends. Simulation efficiency also typically requires the use of significantly reduced versions of kinetic mechanisms.

Development of these reduced, yet accurate, chemical kinetic mechanisms is enabled by experimental input data and validation through a range of devices, including shock tubes, rapid compression machines, flow reactors, and constant volume combustion chambers. Experimental measurements are especially important to highlight and validate ignition performance when combining kinetic mechanisms for different chemical classes to represent a fuel blend. Novel fuel blending components can affect ID performance in non-linear and varying antagonistic or complimentary degrees over temperature, pressure, and equivalence ratio space. Fuel kinetic mechanism development and validation therefore benefits from experimental mapping of ID performance of fuel blends over engine-relevant parametric space.

Approach

NREL's ignition kinetics research builds on continual development and modification of the IQT as a flexible research platform, both for experiments and as a simulation platform for evaluating kinetic mechanisms against experimental data [2–5]. The IQT is a CVCC apparatus with a spray injection system designed for direct measurement of the ignition delay of liquid fuels under engine-relevant temperatures and pressures. The current research on gasoline-range fuels leverages NREL's prior development of novel techniques to conduct ID studies over temperature sweeps at various fixed pressures, which are now used by other IQT users. Inherently longer ID times typical of gasoline-range fuels allowed better mixing, reduced spray physics to affect only a small portion of the overall ID (focusing more on chemical kinetics dominated ID), and enabled studies at higher pressures relevant to engine operation. As a result, NREL's modified IQT produces engine-relevant ignition kinetic data for gasoline-range compounds and blends, filling data voids and overlapping some conditions covered by rapid compression machines and shock tubes. FY 2016 research focused on primary reference fuels (PRFs), toluene standardization fuels, blends of ethanol into iso-octane and PRFs [6]. The detailed ID studies of ethanol blended into well-established reference fuel blends provides a comparative baseline to

study blends of other oxygenated functional groups for Co-Optima boosted SI fuel. In addition, NREL studied ignition performance for a wide range of fuel candidate compounds and research gasoline blends. NREL also recently expanded beyond IQT-based experimental studies, with the internally funded acquisition of a more flexible AFIDA.

NREL's approach includes strong collaboration, including two faculty joint appointments from Colorado School of Mines and a graduate student intern from the University of Colorado Boulder tied to this research. NREL is sharing ID data with other researchers and has been active in applying these techniques to fuel samples shared from other DOE laboratory and industry partners, including a Coordinating Research Council Advanced Vehicles, Fuels, and Lubricants (AVFL) project known as AVFL-30 [7]. Experimental data and IQT simulations with kinetic mechanisms under development are also shared in close collaboration with Lawrence Livermore National Laboratory (LLNL). These collaborations are critical to integrating IQT and AFIDA based data as part the development feedback loop for kinetic mechanisms, correlating temperature and pressure parametric ID sweeps to engine studies, and developing potential for simple CVCC techniques to provide faster screening and ignition performance insight for biofuel candidate blends.

Results

Ignition Kinetics Studies of Ethanol Blends

Since ethanol is known to have non-linear octane blending behavior in gasoline, it was similarly expected that non-linear ignition kinetics effects could be seen for ethanol blends into gasoline surrogates. Accurately capturing these blending behaviors in a kinetic mechanism is critical to effectively simulating advanced gasoline direct injection SI or low temperature combustion strategies such as gasoline compression ignition. NREL conducted an ID study in the IQT assessing the impact of increasing ethanol concentration on the ignition behavior of blends with a particular focus on the changes in LTHR and the NTC region. NTC behavior, critical to fuel ignition performance in the engine, was observed for the first time with iso-octane/ethanol blends using the IQT. Temperature sweeps of iso-octane/ethanol volumetric blends (100/0, 90/10, 80/20, 50/50, and 0/100) were conducted from 623 K to 993 K at 0.5 MPa, 1.0 MPa, and 1.5 MPa and global equivalence ratios ranging from 0.7 to 1.0. Ignition of the iso-octane/ethanol blends was also modeled using a zero-dimensional homogeneous batch reactor to develop more fundamental insight into the underlying reaction dynamics and to assist in feedback development for a gasoline blend surrogate mechanism

including ethanol. The experimental study provided new ethanol blend data for the research community, including blending effects on NTC and LTHR that were presented for the first time. Figure 1 highlights a few of the significant observations of this study, including:

- NTC behavior was observed for iso-octane/ethanol fuel blends up to 20% ethanol.
- Ethanol produced shorter ID times than iso-octane in the high temperature region.
- The initial increase in ethanol from 0% to 10% had a lesser impact on ignition delay than increasing ethanol from 10% to 20%.
- The zero-dimensional model predicts that at 0.5 MPa and 1.0 MPa ethanol produces the shortest ID time in the high temperature regime, as seen experimentally (confirming accuracy of the LLNL gasoline surrogate blend mechanism with ethanol).

Tools for Reduced Mechanism Development

A related study focused on iso-octane as a critical gasoline surrogate component, as a test case for developing faster IQT simulations and supporting development of reduced mechanisms. IQT ID experiments were conducted between temperatures of 653 K and 996 K, pressures of 1.0 MPa and 1.5 MPa, and global equivalence ratios of 0.7 and 1.05. Clear NTC behavior was demonstrated at both pressures in the experimental data, which were used to characterize the effectiveness of three modeling methods for the IQT: a single-zone homogeneous batch

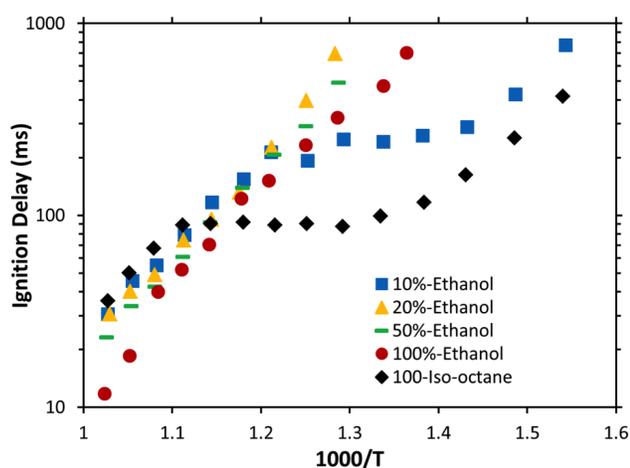


Figure 1. Constant mass injection temperature sweeps at 1.0 MPa are shown with data plotted every 25 K. A 10% ethanol blend increases ID compared to iso-octane, but it maintains NTC region behavior. A 20% blend exhibits much higher ID, more than a 50% blend or even neat ethanol.

reactor, a multizone engine model (based on prior LLNL research), and a three-dimensional CFD model [8]. A detailed 874 species iso-octane mechanism (LLNL) was reduced to 89 species for use in these models, and the predictions of the reduced mechanism were consistent with ignition delay times predicted by the detailed chemical kinetic mechanism across the broad experimental parametric space [9]. The calculations predicted that the main part of the IQT chamber was fairly well mixed at longer times (>30 ms), suggesting that simpler models might be applicable in this quasi-homogenous region. Multizone simulations with 20 zones of temperature and equivalence ratio were quite close to the coupled CFD–kinetics results, but the calculation time was ~ 11 times faster than the coupled CFD–kinetics model. The speed of the multizone IQT model makes it feasible to quickly evaluate more detailed kinetic mechanisms against experimental data than reduced mechanisms typically required for CONVERGE coupled CFD–kinetics simulations.

Advanced Fuel Ignition Delay Analyzer

NREL recently acquired a dedicated research-grade AFIDA CVCC, currently one of four in the world (see Figure 2). The AFIDA offers greater pressure and temperature capability than the IQT, up to 5 MPa and 1,000 K. It also uses a modern high-pressure (1,200 bar) piezo-electric fuel injector that addresses an experimental limitation in the IQT tied to low boiling point fractions

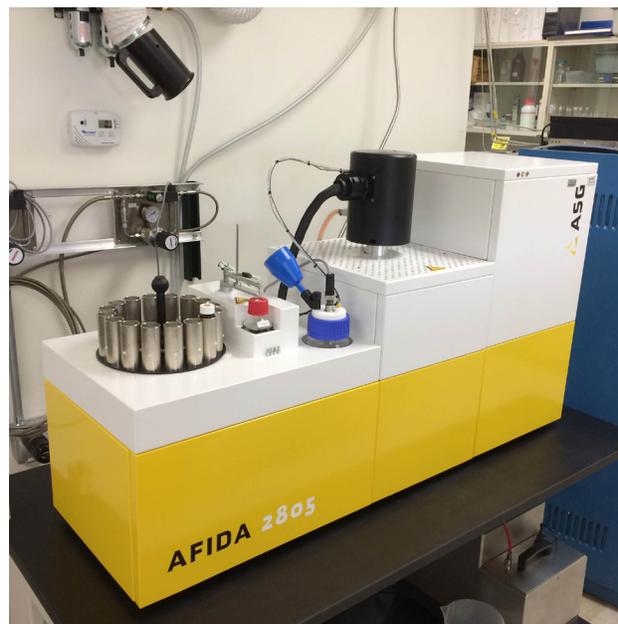


Figure 2. NREL's new research-oriented Advanced Fuel Ignition Delay Analyzer (photo credit Brad Zigler, NREL)

of gasoline blends. The AFIDA's fuel injection system is capable of varying dynamically to hold constant equivalence ratio across a temperature sweep, and also significantly increases mixing and reduces the portion of ID tied to spray physics, greatly increasing focus on chemical kinetics ID. The AFIDA is equipped with a 16-place autosampling carousel, with fuel sample heating and cooling capability. NREL characterized the new AFIDA CVCC for "air" charge filling over its range of pressures and temperatures, as well as variable fuel mass injection control. Initial experiments with a full boiling range research gasoline surrogate blend, Coordinating Research Council Fuels for Advanced Combustion Engines (FACE)-B demonstrate that the AFIDA solves fuel-boiling issues at higher temperatures that limit experiments in the IQT. NREL has begun CFD simulation effort, and will transition most ignition kinetics experiments to the AFIDA in FY 2017.

Conclusions

- IQT and AFIDA CVCC experiments quantify fuel component, surrogate blend, and full boiling range gasoline ignition performance over engine-relevant parametric space.
- Unique IQT and AFIDA 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, toluene standardization fuels, and simple ethanol blend work sets the stage to expand to other oxygenated functional groups, complex surrogate blends, and full boiling range gasoline 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).
- Initial device characterization and experimental studies with the AFIDA demonstrate expanded capability to extend beyond IQT-based studies for high-quality ignition kinetics experiments and simulations.
- Numerical simulation permits IQT, and soon AFIDA, experiments to be part of the feedback loop for development of reduced kinetic mechanisms.
- FY 2016 collaborations included:
 - LLNL – Data for kinetic mechanism development feedback
 - Argonne National Laboratory – Fuel ignition behavior impacts on gasoline compression ignition
 - Pacific Northwest National Laboratory – Biofuel component and complex blend screening and preliminary ignition performance studies
 - University of Michigan – Ignition kinetics experiments for ethanol blends
 - CRC – AVFL-30 project
- The FY 2016 research feeds directly into Co-Optima FY 2017 research.

References

1. Livengood, J.C., and P.C. Wu. "Correlation of autoignition phenomena in internal combustion engines and rapid compression machines." *Symposium (International) on Combustion*. Vol. 5. No. 1. Elsevier, 1955.
2. 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.
3. 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.
4. 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.
5. G. Bogin, A.M. Dean, M.A. Ratcliff, J. Luecke, and B.T. Zigler, "Expanding the Experimental Capabilities of the Ignition Quality Tester for Autoigniting Fuels," *SAE International Journal of Fuels and Lubricants*, Vol. 3, Issue 1, 353–367, 2010.
6. 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>.
7. Coordinating Research Council 2016 Annual Report, Coordinating Research Council, Alpharetta, GA, September 2016.

8. Aceves, S., Flowers, D., Matinez-Frias, J., Smith, J.R., Westbrook, C.K., Pitz, W.J., Dibble, R., Wright, J.F., Akinyemi, W.C., and Hessel, R.P., "A Sequential Fluid Mechanic Chemical-Kinetic Model of Propane HCCI Combustion", SAE 2001-01-1027, 2001.
9. Mehl, M., Curran, H.J., Pitz, W.J., and Westbrook, C.K., "Chemical Kinetic Modeling of Component Mixtures Relevant to Gasoline," *Proceedings of the European Combustion Meeting*, Vienna, Austria, April 14–17, 2009.
3. Brad Zigler, Jon Luecke, Greg Bogin, Eric Osecky, Drew Cameron, Matt Ratcliff, Stephanie Villano, and Tony Dean, "Parametric Ignition Characterization Studies for Alternative Fuels and Blends," presentation at the Advanced Engine Combustion Memorandum of Understanding (MOU) Review Meeting, USCAR, Southfield, MI, August 18, 2016.
4. Robert L. McCormick, Gina Fioroni, Jim Szybist, Tim Bays, Paul Miles, Matt McNenly, Bill Pitz, Jon Luecke, Matt Ratcliff, Brad Zigler, and Scott Goldsborough, "Co-Optimization of Fuels and Engines (Co-Optima) -- Fuel Properties and Chemical Kinetics and Thrust I Engine Projects," presented at DOE Vehicle Technologies Annual Merit Review, Washington, D.C., June 9, 2016.

FY 2016 Publications/Presentations

1. Gregory E. Bogin Jr., Jon Luecke, Matthew A. Ratcliff, Eric Osecky, Bradley T. Zigler, "Effects of Iso-octane/Ethanol Blend Ratios on the Observance of Negative Temperature Coefficient Behavior within the Ignition Quality Tester," *Fuel*, Volume **186**, 15 December 2016, Pages 82–90, ISSN 0016-2361, <http://dx.doi.org/10.1016/j.fuel.2016.08.021>.
2. Eric M. Osecky, Gregory E. Bogin, Jr., Stephanie M. Villano, Matthew A. Ratcliff, Jon Luecke, Bradley T. Zigler, and Anthony M. Dean, "Investigation of Iso-octane Ignition and Validation of a Multizone Modeling Method in an Ignition Quality Tester, *Energy & Fuels* **2016** 30 (11), 9761-9771, DOI: 10.1021/acs.energyfuels.6b01406.
5. Brad Zigler, Jon Luecke, Greg Bogin, Matt Ratcliff, and Bob McCormick, "Alternative Fuel Ignition Characterization Studies," presentation at the Advanced Engine Combustion MOU Review Meeting, Sandia National Laboratories, Livermore, CA, February 10, 2016.

V. Lubricants to Enable High Engine and Vehicle Fuel Efficiency

The Fuel & Lubricant Technologies subprogram 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. This research leverages the national laboratories' unique capabilities and facilities to conduct fundamental studies on tribology, the science of friction and wear. To enable further developments in these areas, research into novel additives and other approaches is supported at universities and additive companies.

V.1 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 and their 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

Fiscal Year (FY) 2016 Objectives

- Measure PAG lubricant friction and wear properties and compare performance to SAE 75W-140 baseline
- Optimize additive package performance
- Demonstrate acceptable durability performance and improved efficiency in system level industry standard lubricant testing

FY 2016 Accomplishments

- System level industry standard thermal oxidative stability testing (ASTM D5704) was completed for the most promising oil soluble PAG (OSP) and Generation II PAG (Gen II PAG) formulations and passed.
- System level industry standard shock load testing (ASTM D7452) was completed for the most promising OSP formulations but failed.
- Dow Chemical Company (Dow) and Ford Motor Company (FMC) analyzed the deficiencies of the OSP formulations that failed shock load testing, and optimized the formulations for extreme pressure performance and antifoam characteristics.

Arup K. Gangopadhyay (Primary Contact)

Ford Motor Company
2101 Village Road
Dearborn, MI 48121
Phone: (313) 322-6986
Email: agangopa@ford.com

Chintan Ved, Nikolaus Jost

Ford Motor Company
35500 Plymouth Road
Livonia, MI 48150
Phone: (313) 805-9495
Email: cved@ford.com

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager:
Nicholas D'Amico

Subcontractors:

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

- Dow and Argonne National Laboratory (ANL) continued with various laboratory bench screening tests for the OSP formulations.

- FMC conducted preliminary efficiency testing on one of the OSP formulations that passed industry standard load carrying capacity testing, that benchmarked PAG performance to 75W-140, confirming efficiency and temperature performance improvements.

Future Directions

- Complete additional industry standard axle system tests, including load carrying capacity, moisture corrosion, oxidative stability, and shock loading testing with top formulation candidates
- Complete FMC proprietary axle system (efficiency and gear wear) testing with top formulation candidates
- Define the best candidate formulation

- Complete chassis roll dynamometer tests for fuel economy and emission evaluations ■

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, solely pursuing efficiency gains by means of viscosity reduction creates concern for axle component durability due to reduced oil film thickness. The PAG approach incorporates viscosity reduction along with chemistry driven friction reduction in order to improve on axle efficiency.

Approach

The project team consists of technical personnel from FMC, Dow, and ANL. The project is led by Arup Gangopadhyay (FMC), Chintan Ved (FMC), Nikolaus Jost (FMC), John Cuthbert (Dow), Ashish Kotnis (Dow), and Dr. Ali Erdemir (ANL). All three partners have key roles in achieving the project objectives. FMC is the prime contractor and provides technical direction to ensure all bench, component, and systems level tests are completed. Dow is instrumental in providing new lubricant formulations and completing physical property testing. ANL is responsible for bench-top friction testing, wear testing, and surface analytical characterization techniques.

The project begins 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 is then to conduct component, dynamometer, and vehicle level testing to assess durability and axle efficiency. The resulting test data is

used to estimate PAG fuel economy benefits and is to be validated with chassis roll fuel economy dynamometer tests.

Results

OSP and Gen II PAG Thermal Oxidative State Testing

After exhibiting successful performance in load carrying capacity testing (ASTM D6121) with two OSP formulations, OSP formulation AW0704-A was selected as the best candidate to continue with system level testing evaluations due to its superior delivery of phosphorous to gear surfaces for wear protection. It was assumed that the Gen II PAG with the corresponding equivalent antiwear additive package, AW0705-F, would perform similarly, thus was selected to continue with system level testing evaluations as well.

The two formulations completed ASTM D5704 Thermal Oxidative State Stability Testing and exhibited passing results presented in Table 1. Table 1 also displays historical reference values for 75W-140 for comparison. The data in Table 1 shows that the change in viscosity for the OSP candidate was less than that for the Gen II PAG, although having a higher initial value. This drove the decision to pursue the OSP as the more stable candidate, as it is intended to develop an end product that can exhibit consistent properties at fresh and aged stages of life.

OSP Shock Load Testing

The post-test evaluation of hardware that completed shock load testing with OSP AW0704-A provided data that demonstrated that the formulation is not suitable as an final drive axle lubricant end product. Significant scoring on both drive and coast side of both ring and pinion gears was present. The ring received an end of test rating of 97% scoring on the drive side, and 92% scoring on the coast side. The pinion received an end of test rating of 77% scoring on the drive side, and 88% scoring on the coast side. Example pictures of the scoring can be seen in Figure 1. The passing limits are 11% on ring drive and coast side, and 18% on pinion drive and coast side.

Table 1. Results from the Thermal Oxidative Stability Testing (ASTM D5704) for Top Candidate OSP and Gen II PAGs

	PAG	Viscosity				Pentane Insolubles, % wt.	Toluene Insolubles, % wt.	Avg. Carbon/Varnish (merits)	Avg. Sludge (merits)
		Initial	50 hr	Change	% Change				
75W-140	--	--	--	--	50%	1.5	1.5	7.5 [minimum]	9.4 [minimum]
AW0704-A	OSP	11.36	11.58	0.22	2	4.69	0	9.5	9.5
AW0705-F	Gen II	10.16	10.86	0.7	7	2.2	0.2	9.8	9.5

The test shows the oil thickening and deposit formation of lubricants at high temperature oxidizing conditions. The 75W-140 row is featured as a reference of historical performance, as testing data was not generated at the same time as for the PAGs.

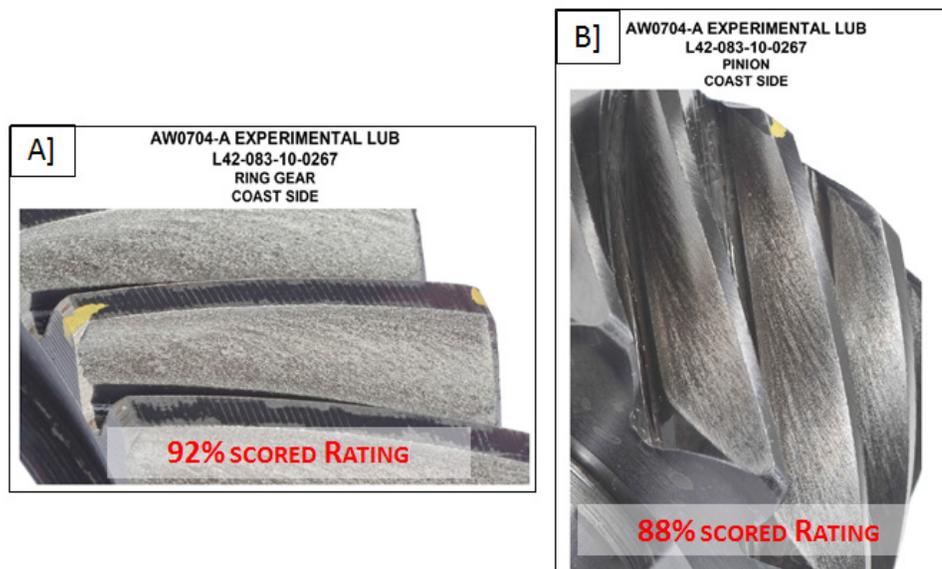


Figure 1. Photographic evidence supplied by Intertek of scoring on post-test hardware tested with OSP AW0704-A following ASTM D7452 shock load testing procedure. The ASTM D452 test is intended to show the anti-scoring properties of axle lubricants in shock loading conditions. Photo A shows the ring gear coast side scoring and Photo B shows the pinion gear coast side scoring.

The extreme pressure performance of OSP AW0704-A formulation was identified as a potential deficiency. Previous bench rig extreme pressure (EP) testing showed the AW0704-A had compromised on the baseline performance of 75W-140. In order to address this deficiency, derivative formulations of OSP AW0704-A were developed, resulting in OSP formulation AW0704-R, which maintained similar performance to AW0704-A in all bench rig screening tests, with exception to EP testing. Matching the performance of AW0704-R, with its predecessor AW0704-A, in bench testing was done under the assumption that the performance in those tests

would correlate to the passing antiwear performance that was exhibited by AW0704-A in the system level load cycling testing that was completed in 2015 [1]. Table 2 presents the data for the comparative performances of the 75W-140, AW0704-A, AW0704-R, and another derivative formulation that was not selected for continued testing in the bench screening tests.

The post-test evaluation of hardware that completed shock load testing with OSP AW0704-R also showed that the formulation is not suitable as a final drive axle lubricant. However, final scoring ratings were improved compared

Table 2. Bench Testing Results for Wear, Extreme Pressure, Oxidative Stability, Rust Prevention and Copper Corrosion for 75W-140, AW0704-A, and its Derivative Formulations

	Formulation Number	Wear Tests			EP Tests		TOST Results		Rust Prevention	Copper Corrosion
		4 Ball wear (mm)	B.O.D. Disc wear (mm)	B.O.D. Ball Wear (mm)	Falex EP (lb)	4 Ball EP (kg)	Δ TAN	Viscosity Increase, %		
Baseline	75W-140	0.42	0.44	0.41	2807 3041	420	1.50	20.0	PASS	2A
OSP	AW0704-A	0.36 0.42	0.32	0.31	2885	315	1.26	3.9	PASS	1B
	AW0704-R	0.49	0.36	0.22	>4500	400	1.8	4.5	PASS	1B
	AW0704-W	0.38	0.35	0.22	4172	315	1.3	5.4	PASS	1B

BOD – ball-on-disc; TOST – Thermal Oxidative Stability Test
 AW0704-R was selected as the best candidate due to its improved EP performance.

to AW0704-A, with drive side scoring reduced to 0% from above 90% for both ring and pinion, thus confirming that the changes in EP performance made in AW0704-R did translate to improved shock loading performance. The ring received an end of test rating of 0% scoring on the drive side, and 33% scoring on the coast side. The pinion received an end of test rating of 0% scoring on the drive side, and 44% scoring on the coast side. Pictures of the scoring can be seen in Figure 2.

OSP Antifoam Improvement

Another factor, initially overlooked, that was determined to be a contributing factor to the failure of both OSP formulations in shock load testing was their antifoaming

performance. Observations of the presence of foam at the end of test were made for both AW0704-A and AW0704-R. Foam tendency testing per ASTM D892 of formulations AW0704-A and AW0704-R proved that both OSP formulations lacked appropriate antifoaming additive function. Table 3 shows the baseline foaming results for AW0704-A and AW0704-R, and two developed formulations with optimized antifoam performance. As shown in Table 3, AW0704-BN exhibited superior antifoaming behavior to the baseline OSP formulations, and was therefore selected to be resubmitted for thermal oxidative stability and shock loading testing. Results are expected in the first quarter of 2017.

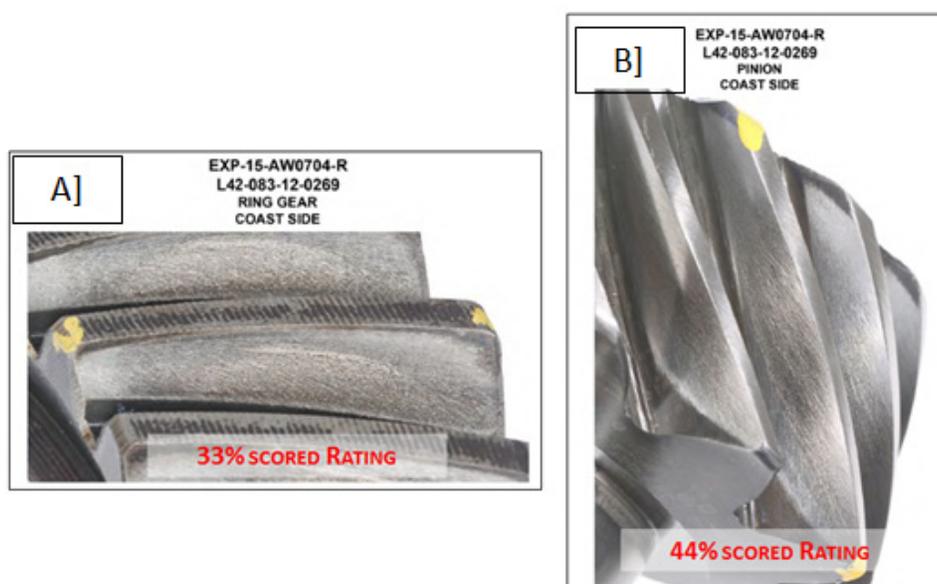


Figure 2. Photographic evidence supplied by Intertek of scoring on post-test hardware tested with OSP AW0704-R following ASTM D7452 procedure. The ASTM D452 test is intended to show the antiscoring properties of axle lubricants in shock loading conditions.

Table 3. Foam Tendency per ASTM D892, Presented in Milliliters

	AW0704-A	AW0704-R	AW0704-BE	AW0704-BN
Sequence I	545	530	170	50
Sequence II	310	630	190	65
Sequence III	545	530	110	40
Sequence IV	640	>950	60	60

OSP formulations AW0704-A and AW0704-R that failed shock load testing showed excessive foaming. The table shows two formulations, AW0704-BE and AW0704-BN, that were developed from an antifoam additive package optimization design of experiments.

OSP Axle System Level Efficiency

FMC conducted axle system level efficiency testing to compare the OSP performance to baseline 75W-140. Efficiency testing was initiated prior to the failure of AW0704-A in shock load testing, so axles were tested with AW0704-A, as it was the best available candidate at the time. The data generated by this testing, although completed with an OSP formulation that is nonviable for use as an end product, does validate that the OSP formulation, which all subsequent formulations have been designed to emulate, does outperform 75W-140 (see Figure 3). The improved efficiency and heat generation reduction suggest that the OSP formulation combines drag loss improvements from viscosity reduction and friction reduction from chemical composition to produce a more favorable system level performance. It is expected to observe similar results when the test is completed with the OSP formulation that has been antifoam optimized.

Conclusions

- The OSP formulation AW0704-A successfully exhibited considerable system level efficiency and temperature improvement when compared to 75W-140 gear oil, meeting an explicit project goal.
- Although AW0704-A was not able to pass shock load testing, modifications were made to optimize EP and antifoaming performance, and are expected to have minimal impact on system level durability and wear performance, due to the strategy to derive all subsequent formulations from AW0704-A and the utilization of performance data in bench screening testing.

References

1. Gangopadhyay, A.; Ved, C; Jost, N. (2016) Development of PAG (Polyalkylene Glycol)-Based Lubricant for Light- and Medium-Duty Axle Applications. DOE 2015 Annual Report Fuel and Lubricant Technologies. 76–79.

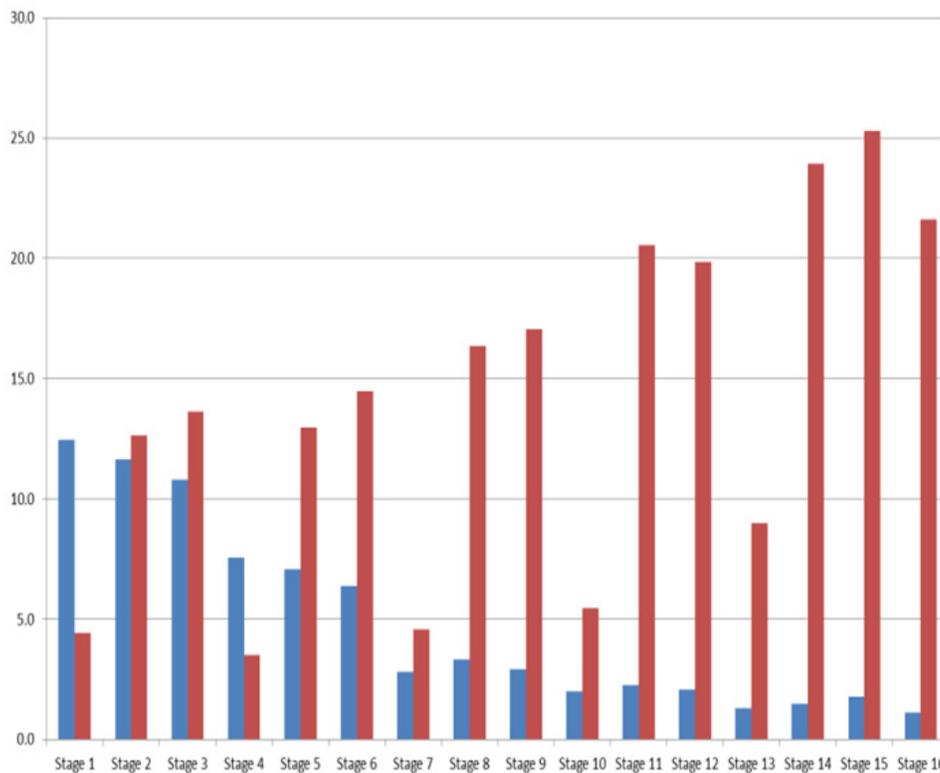


Figure 3. Depicted are the differences between OSP AW0704-A and baseline 75W-140 in percent efficiency and temperature (°F) at various stages of FMC proprietary axle testing. The bars in blue (■) are representative of the percent efficiency of AW0704-A minus the percent efficiency of 75W-140 at each respective stage. The bars in red (■) are representative of the axle temperature of 75W-140 minus the axle temperature of AW0704-A at each respective stage.

V.2 Power Cylinder Friction Reduction Through Coatings, Surface Finish, and Design

Overall Objectives

- Develop and demonstrate friction reduction technologies for light- and medium-duty vehicles that improve fuel efficiency of future vehicles by at least 4% over currently used technologies based on comparative results from chassis dynamometer testing without adverse impacts on vehicle performance or durability
- Achieve objective using new materials and low friction coatings, improved finish, design, and novel engine oil formulation

Fiscal Year (FY) 2016 Accomplishments

- Identified coating deposition parameters that meet targeted plasma transferred wire arc (PTWA) coating porosity levels (6–8%) and established repeatability
 - Identified honing techniques that exceed targeted porosity levels offering great flexibility
 - Thoroughly characterized coatings for percent porosity, percent oxide content, and hardness
 - Developed manufacturing methodology to deposit coatings on freestanding liners (for laboratory bench tests and characterization), liners (for component level friction tests), and engine blocks (for engine friction tests)
 - Showed up to 50% reduction in friction coefficient in mixed lubrication regime in initial laboratory bench tests
 - Deposited nano-composite vanadium nitride (VN)–Cu coating on piston rings; laboratory bench friction and wear tests conducted with two different engine oil formulations
 - Demonstrated friction reduction potential of micro-polished crank journal in progress with GF-5 oil and polyalkylene glycol engine oils using a motored cranktrain rig
- Demonstrate if VN–Cu nano-composite coating on rings offer friction reduction in contact with PTWA coated liners
 - Quantify friction reduction with micro-polished crank journals
 - Demonstrate friction reduction in pressurized single-cylinder engine
 - Demonstrate friction reduction in multi-cylinder engine block (cranktrain rig)
 - Initiate wear assessment of PTWA coating in motored engine tests ■

Future Directions

- Repeat laboratory friction tests to understand if pore size distribution influences friction reduction

Dr. Arup K. Gangopadhyay (Primary Contact)

Ford Motor Company
2101 Village Rd.
Dearborn, MI 48121
Phone (313) 322-6986
Email: agangopa@ford.com

Dr. Ali Erdemir

Argonne National Laboratory
9700 Cass Avenue, Building 212
Argonne, IL 60439
Phone (630) 252-6571
Email: erdemir@anl.gov

DOE Technology Development Manager:
Michael Weismiller

NETL Project Manager:
Adrienne Riggi

Introduction

About 7–10% of the total energy input in a vehicle is lost due to mechanical friction [1], and therefore offers great opportunities for friction reduction. Figure 1 shows about 60% of the total frictional losses in an engine occur at the interface between the cylinder, pistons, and piston rings and about 30% loss at the bearings [2].

The goal of this project is to demonstrate the friction reduction capabilities of advanced coatings, surface finish, and design on a power cylinder system containing cylinder bore, piston rings, piston skirt, bearings, and crankshaft with advanced engine oils. Ford believes the full friction reduction benefit can only be reached using a systems approach.

Approach

The research proposal focused on several components in an engine power cylinder system:

- Cylinder bore surface: deposit a ferrous-based, high porosity, coating using a PTWA process. Low porosity PTWA coatings have been introduced in a few mass produced engines [3] but have not necessarily offered reduced friction. However, some evidence indicates a high porosity (6–8%) coating may offer the friction benefit needed [4].
- Bore finish: explore the effect of reducing surface roughness from 0.3 μm to below 0.2 μm Ra (average roughness).
- Piston ring coatings: investigate at least three coatings to reduce friction; chromium nitride, diamond-like carbon, and nano-composite.

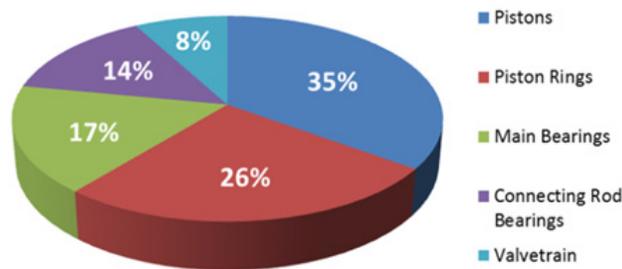


Figure 1. The distribution of frictional losses in an engine

- Crankshaft: reduce friction by micro-polishing crankshaft journals; from current state of Ra = 0.10 μm to 0.04 μm.
- Lubricants: use polyalkylene glycol-based engine oil formulations developed from a previous DOE funded project.

Results

Budget Period 1 focused on identifying critical plasma torch parameters and levels for depositing PTWA coatings with the desired level of porosities and critical parameters for honing liner surface. Three levels of porosities were targeted (<2%, 3–5%, 6–8%) and the selection of critical parameters helped to exceed these limits.

Budget Period 2 started with duplicating the parameters to ensure coating porosity level and finished surface could be consistently manufactured. Figure 2 shows micrographs of PTWA coatings with various levels of porosities. These liners were characterized at the top, middle, and bottom sections for porosity levels, oxide content, and hardness.

Figure 3 shows hardness data for various coating deposition conditions. A majority of the coatings were deposited with low carbon steel wire (1010) as feedstock, while a few used medium carbon steel wire (1080). The effect of shrouding gas (air or nitrogen) and torch design (Nozzle 1 and Nozzle 2) were also explored. The hardness values for different coatings were measured to be from 244 HV to 476 HV. The hardness of cast iron liner is typically 300 HV. As expected coatings deposited with medium carbon steel wire exhibited higher hardness because of higher carbon content.

The final coating deposition and honing parameters were used on aluminum liners for evaluating laboratory bench test friction, motored single-cylinder piston ring friction, and engine blocks for motored multi-cylinder friction. All these liners were thoroughly inspected for cylindricity,

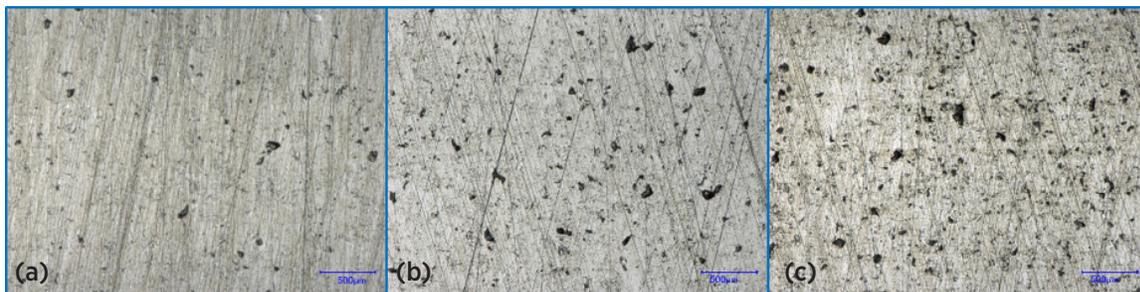


Figure 2. Examples of different levels of porosity achieved on the PTWA coating. (a) Porosity less than 2.0%, (b) porosity within 3.0–5.0%, and (c) porosity within 6.0–8.0%.

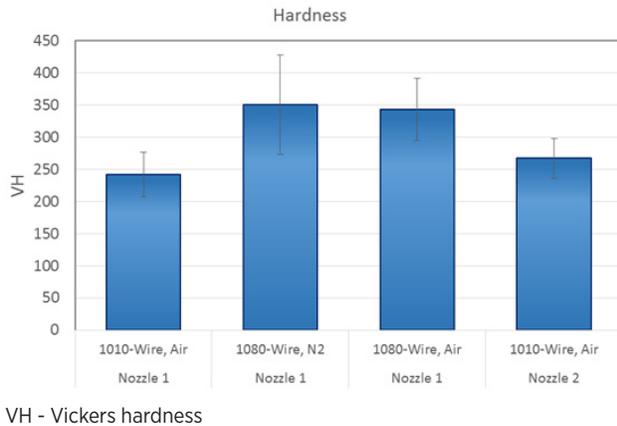


Figure 3. Hardness of various high porosity PTWA coatings

and out of roundness to ensure all were within acceptable range to avoid any influence on the friction results.

Some of these liners were sectioned and used to complete a reciprocating laboratory test rig (Plint TE-77) friction evaluation; a test where a section of a piston ring is reciprocated against a stationary liner section while submerged in GF-5 SAE 5W-20 oil maintained at specified temperatures. The change in the coefficient of friction as a function of product of lubricant viscosity (μ) and ring velocity (V) is shown in Figure 4. The PTWA coating (Test 22) showed a coefficient of friction reduction up to 50% under mixed lubrication regime compared to the cast iron material (Test 30).

Friction and wear tests were also completed on a nano-composite (VN-Cu) coating developed by Argonne National Laboratory using a dual magnetron sputtering system. The test was performed using a high frequency reciprocating rig in which a section of a coated piston ring is reciprocated against a stationary liner section submerged in GF-5 SAE 5W-20 oil at 120°C and a frequency of 10 Hz for 24 h. Figure 5 shows no

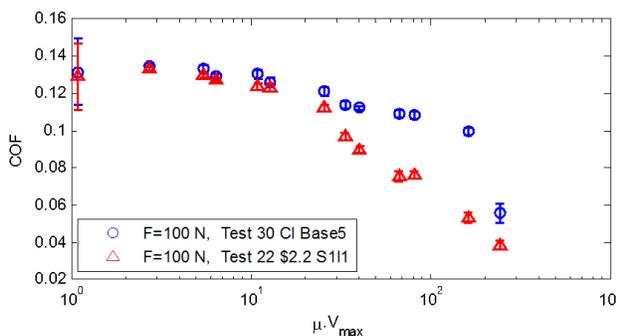


Figure 4. Coefficient of friction (COF) as a function of lubricant viscosity x velocity for cast iron liner, and high porosity PTWA

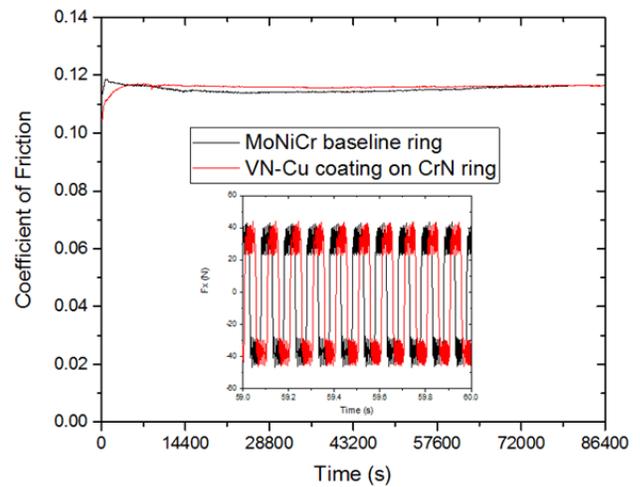


Figure 5. Coefficient of friction as a function of test duration for baseline piston ring with Mo-NiCr and VN-Cu nanocomposite

significant friction difference in VN-Cu compared to the Mo-NiCr coating. These results are most likely due to the high friction provided by the dominating antiwear tribofilm produced by the 5W-20 oil additives.

Figure 6 shows evidence of improved wear resistance of the nano-composite compared to the Mo-NiCr coating. The nanocomposite coating does not show evidence of wear, but instead shows the formation of a colorful surface tribofilm. Evidence of wear can be observed on the Mo-NiCr coating by the disappearance of the original polishing marks. Unfortunately, the quantification of wear is quite difficult due to very low mass loss (less than 0.05 g) and possible mass gain due to entrapment of lubricant in the pores.

Conclusions

A number of achievements were completed during Budget Period 2. The team developed a manufacturing method for depositing a high porosity coating and honing process. The process was shown to repeatedly achieve targeted porosity levels. Additionally, the significant friction reduction capability of high porosity PTWA coatings compared to cast iron liners was demonstrated, as well as the improved wear resistance of a VN-Cu nano-composite coated ring compared to a Mo-NiCr coating.

References

1. O. Pinkus, and D.F. Wilcock, "Strategy for energy conservation through tribology," New York, ASME, 1977.

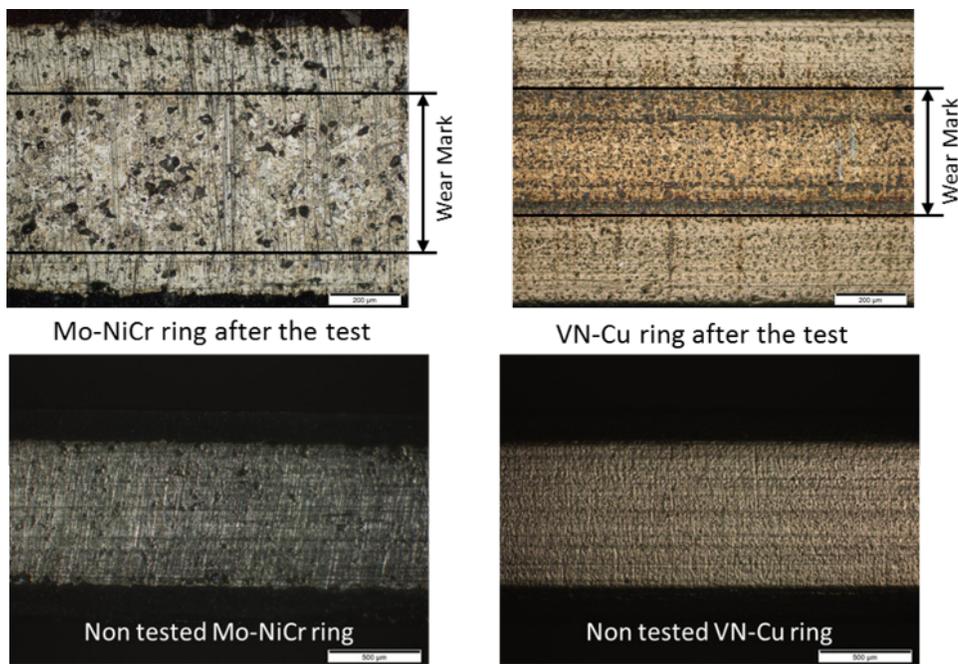


Figure 6. Wear comparison of the rings coated with VN-Cu nano-composite and Mo-NiCr coatings

2. T.E. Kiovsky, N.C. Yates, and J.R. Bales, “Fuel efficient lubricants and the effect of base oils,” *Lubrication Engineering*, April 1994.
3. B. Gand, “Coating for cylinder surfaces in aluminium engine blocks,” *MTZ*, 201172, pp 34–39.
4. U. Morawitz, J. Mehring, and L. Schamm, “Benefits of thermal spray coatings in internal combustion engines with specific view on friction reduction and thermal management,” SAE paper no. 2013-01-0292, 2013.

FY 2016 Publications/Presentations

1. “Development and characterization of a high surface porosity thermally sprayed coating,” submitted for presentation at the STLE Annual Meeting, Atlanta, May 21–25, 2017.

Special Recognitions and Awards/ Patents Issued

1. “Low cost thermal spray coating for improved engine performance,” submitted patent application, March 18, 2016.

V.3 Hybrid Ionic-Nano-Additives for Engine Lubrication to Improve Fuel Efficiency

Overall Objectives

- Develop hybrid nanoparticle (NP) lubricant additives for friction and wear reduction to improve engine energy efficiency via synergistic combination of NPs with oil-soluble ionic liquids (ILs), organic ligands, and polymer brushes
- Demonstrate 10% reduction in engine mechanical energy loss using hybrid NP-additized lower viscosity engine oils

Fiscal Year (FY) 2016 Objectives

- Synthesize oil-soluble IL, organic ligand- and polymer-functionalized NPs
- Demonstrate the dispersibility and stability of hybrid NPs in polyalphaolefin (PAO) 4 cSt base oil
- Achieve significant reduction in friction and wear compared with PAO
- Conduct modeling to investigate NP effects on friction

FY 2016 Accomplishments

- Synthesized oil-soluble IL-functionalized silica NPs (IL-SiO₂NPs) and achieved ~50% friction reduction and ~80% wear reduction at ambient conditions when 1% IL-SiO₂NPs were added into PAO
- Developed oil-soluble polymer-grafted silica and titania NPs (hairy NPs) that exhibited long-term stability in PAO at -20°C, 22°C, and 100°C (≥55 d) and demonstrated significant friction reduction (up to ~40%) and wear reduction (up to ~90 %) with the addition of 1% hairy NPs into PAO
- Synthesized 1–6 nm organic ligand-functionalized silver NPs and achieved up to 35% friction reduction and 80% wear reduction by adding silver NPs (≤0.5%) to PAO
- Revealed the dependence of tribological effect of NPs on the ratio of NP size to the initial surface roughness of counter surfaces by computer simulations

Future Directions

- Investigate the effect of polymer chemical composition on hairy NPs' tribological performance

Bin Zhao (Primary Contact), Sheng Dai, Roger Wright, Kewei Wang, and Bryan Seymour

University of Tennessee
1420 Circle Drive
Knoxville, TN 37996-1600
Phone: (865) 974-3399
Email: bzhao@utk.edu

Jun Qu, Humin Luo, Beth Armstrong, Chanaka Kumara, and Yu Xie

Oak Ridge National Laboratory
P.O. Box 2008, MS-6063
Oak Ridge, TN 37831-6063
Phone: (865) 964-3025
Email: qujn@ornl.gov

Ashlie Martini and Hongyu Gao

University of California Merced
5200 North Lake Rd
Merced, CA 95343
Phone: (209) 228-2354
Email: amartini@ucmerced.edu

DOE Technology Development Manager:
Michael Weismiller

NETL Project Manager:
Nicholas D'Amico

- Develop IL-functionalized NPs and hairy NPs that exhibit improved lubricating properties and long-term stability in PAO
- Explore different types of core NPs for preparing hybrid NP additives
- Elucidate lubrication mechanisms of hybrid NPs by both experimental and modeling studies ■

Introduction

For an internal combustion engine, 10–15% of the fuel energy is lost to parasitic friction. Using lower viscosity

lubricating oils can improve the fuel efficiency, but poses challenges for wear protection. NPs have been suggested to have good potential as effective lubricant additives for friction and wear reduction. However, the main problem with NPs as lubricant additives is their dispersibility and long-term stability in lubricating base oils. Despite that various methods have been tested to disperse NPs, achieving the full potential of NPs as lubricant additives remains a great challenge.

Approach

The approach used in this project is to synthesize oil-soluble hybrid NPs via synergistic combination of NPs with oil-soluble ILs, organic ligands, and polymers. Oil-miscible ILs are another promising class of lubricant additives. Functionalization of NPs with ILs, organic ligands, and polymers is expected to produce hybrid NPs with excellent tribological properties and stability in PAO. The work scope includes: (1) synthesis of oil-soluble IL-, organic ligand-, and polymer-grafted NPs; (2) study of hybrid NP's dispersity and stability in PAO; (3) tribological testing and analysis; (4) elucidation of lubrication mechanisms of hybrid NPs by experimental and modeling studies; and (5) multi-cylinder fired engine fuel efficiency dynamometer tests.

Results

Oil-soluble IL-modified silica NPs (IL-SiO₂NPs) were synthesized and confirmed by thermogravimetric analysis.

Transmission electron microscopy study showed that the average size of the IL-SiO₂NPs was 17 nm. The freshly prepared IL-SiO₂NPs can be readily dispersed in PAO by ultrasonication, forming transparent dispersions, which were stable at room temperature for months without any precipitation. The tribological properties of IL-SiO₂NPs were studied at a concentration of 1.0 wt% using a Plint TE-77 tribo-tester in a ball-on-flat (52100 steel ball against CL35 cast iron flat) reciprocating configuration at room temperature with a normal load of 100 N. The results showed that the addition of 1% IL-SiO₂NPs into PAO reduced the friction coefficient by ~50% and wear by ~80%, indicating that hybrid IL-NPs are promising lubricant additives. However, at 100°C, scuffing was observed, and the reason is still unclear.

By using surface-initiated polymerization, a series of oil-soluble poly(lauryl methacrylate) brush-grafted NPs (entries 1–7 in Table 1) from 23.8 nm silica NPs and 15 nm titania NPs were synthesized. These polymer brush-grafted NPs (i.e., hairy NPs) can be well dispersed in PAO, forming clear dispersions; no changes were observed after being kept at –20°C, 22°C, and 100°C for ≥55 d (Figures 1A–1D). The tribological properties of hairy NPs were studied as for IL-SiO₂NPs except at 100°C (Figure 2). The addition of 1 wt% hairy NPs into PAO greatly improved the lubricating performance; for both silica and titania NPs, there was a general trend that the coefficient of friction decreased with decreasing brush molecular weight. The coefficient of friction was reduced by ~30% for HNP-SiO₂-4.1k and by ~40%

Table 1. Characterization Data for Oil-Soluble Polymer Brush-Grafted Silica and Titania NPs and Corresponding Free Polymers

Entry	Hairy NPs	DP	M _{n,SEC} (kDa)	PDI	Grafting Density (chains/nm ²)
1	HNP-SiO ₂ -38.0k	117	38.0	1.09	0.72
2	HNP-SiO ₂ -21.7k	66	21.7	1.10	0.72
3	HNP-SiO ₂ -11.8k	31	11.8	1.13	0.72
4	HNP-SiO ₂ -4.4k	5	4.1	1.14	0.67
5	HNP-TiO ₂ -21.5k	66	21.5	1.10	1.27
6	HNP-TiO ₂ -16.2k	57	16.2	1.12	0.83
7	HNP-TiO ₂ -8.1k	22	8.1	1.16	0.80
8	HNP-SiO ₂ -PC13-SP+	30	-	-	0.38

PDI – polydispersity index; DP – degree of polymerization; M_{n,SEC} – number average molecular weight

for HNP-TiO₂-8.1k relative to neat PAO. In addition, all samples showed a marked decrease in wear (>90% reduction in wear for the two lowest molecular weight hairy titania samples). The formation of tribofilms was confirmed by transmission electron microscopy.

To study the effect of chemical composition of polymer brushes on tribological performance of hairy NPs, a series of hybrid NPs composed of a silica NP core grafted with various poly(alkyl methacrylate) brushes were prepared. Preliminary studies indicated that the solubility and stability of these hairy NPs in PAO depended on the alkyl length of the grafted polymer, which was reproduced in atomistic simulations. Incorporating IL moieties into hairy NPs is expected to further reduce friction and wear. By surface-initiated copolymerization of tridecyl methacrylate and bis(trioctyl(4-vinylbenzyl)phosphonium bis(2-ethylhexyl)phosphate (SP+), we synthesized IL-containing hairy NPs (HNP-SiO₂-PC13-SP+, entry 8 in Table 1). The molar content of SP+ in the copolymer was

8.4%. HNP-SiO₂-PC13-SP+ can be dispersed in PAO, forming clear and stable dispersions (Figures 1E and 1F).

We also synthesized 1–6 nm silver NPs functionalized with 4-(*tert*-butyl)benzyl thiol (TBBT) and dodecanethiol (C12). Figure 3 shows the Ag NP-TBBT of <3 nm, 4.5 nm Ag NP-TBBT, and 4.5 nm Ag NP-C12.

Tribological tests were performed on the Ag NP-additized PAO using a Plint TE77 tribometer in a configuration of an American Iron and Steel Institute 52100 steel ball reciprocating sliding against an M2 tool steel flat. Figure 4A shows the friction traces of PAO and the oils containing Ag NPs at room temperature. The two Ag NP-TBBT samples performed similarly with ~35% friction reduction while the Ag NP-C12 NPs showed ~15% friction reduction compared to neat PAO. The addition of Ag NPs also reduced the wear, and the larger NPs were more effective in wear protection than the smaller ones. Energy dispersive X-ray spectroscopy analysis shows the presence of silver and sulfur on the worn surfaces, indicating the deposition of silver NPs on

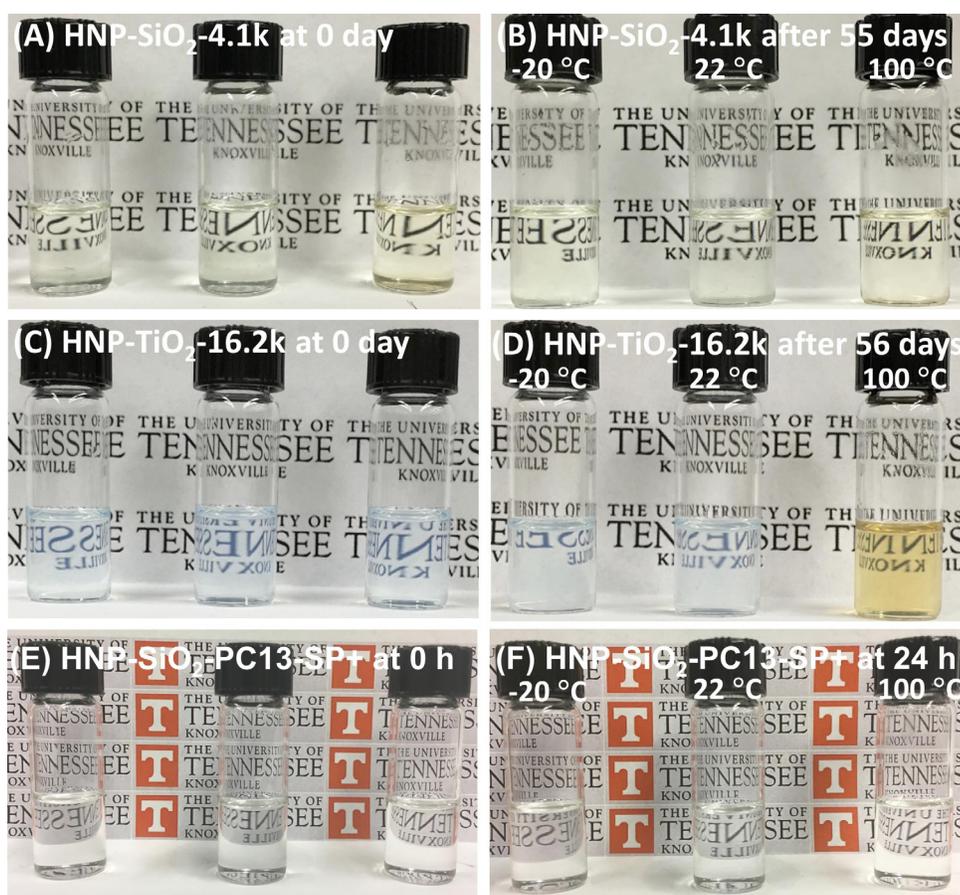


Figure 1. Stability of 1 wt% hairy NPs in PAO at various temperatures after a period of time

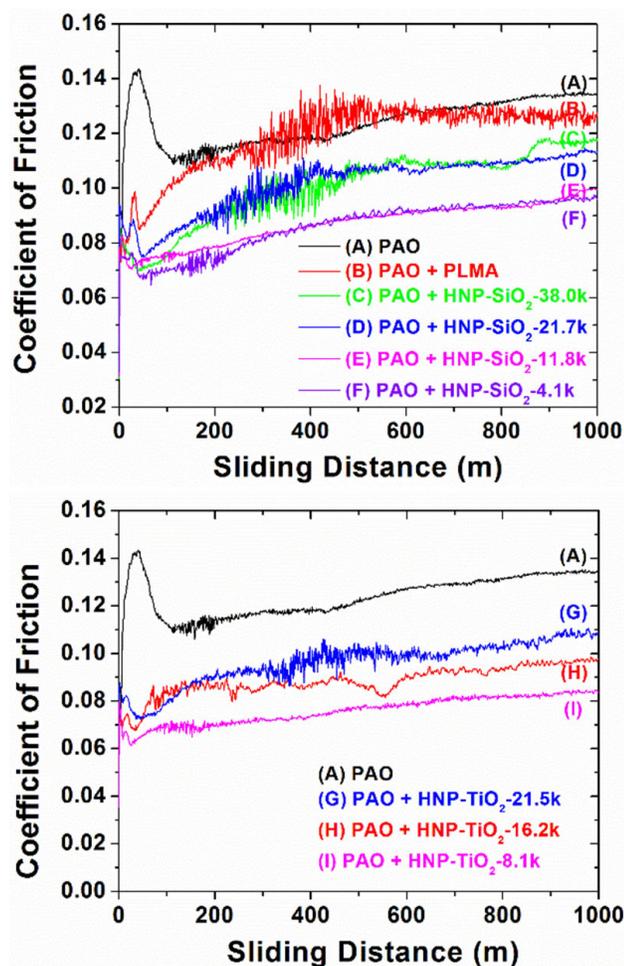


Figure 2. Friction curves for (A) PAO, (B) PAO containing 1 wt% of free poly(lauryl methacrylate), (C) HNP-SiO₂-38.0k, (D) HNP-SiO₂-21.7k, (E) HNP-SiO₂-11.8k, (F) HNP-SiO₂-4.1k, (G) HNP-TiO₂-21.5k, (H) HNP-TiO₂-16.2k, and (I) HNP-TiO₂-8.1k.

the contact area, which was presumably responsible for the friction and wear reduction. Similar tribological tests at 100°C, however, failed to show such an improvement in coefficient of friction when silver NPs were added.

Some literature suggested that NPs may act as microscopic bearing balls at contact interfaces to transition sliding to rolling motion, thus reducing friction and wear. To test this hypothesis, a variable load-speed bearing tester under a cylinder-on-flat unidirectional sliding configuration was used to study the friction behavior of Ag NP-additized oils. A cylinder of American Iron and Steel Institute 8620 alloy steel was set to rotate against a M2 steel flat under a normal load of 50 N. The sliding speed varied from 1.2 m/s to 0.1 m/s at a 0.1 m/s interval. The Stribeck curves generated without and with Ag NPs are compared in Figure 4B, which showed little

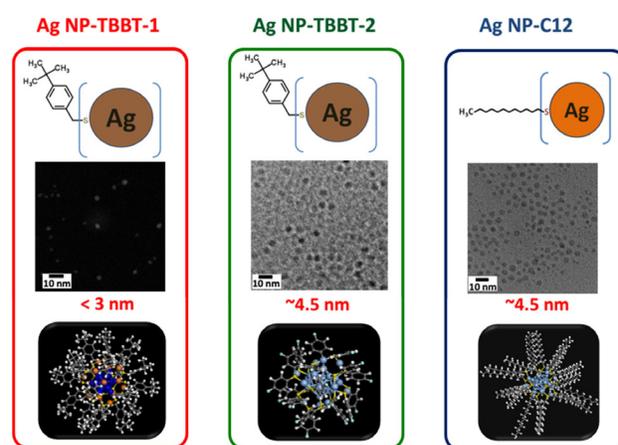


Figure 3. Structures of Ag NP-TBBT-1 of <3 nm, ~4.5 nm Ag NP-TBBT-2, and ~4.5 nm Ag NP-C12. Lowermost images show the models developed for molecular dynamics simulation.

change in friction behavior upon addition of NPs. No Ag deposition was detected in the worn area. This suggests neither significant NP rolling effect (probably because the Ag NPs are much softer than the steel surface) nor NP smearing (likely due to the relatively low pressure in the test).

Molecular dynamics simulations of TiO₂ NPs revealed that another important parameter in determining tribological properties of NPs is the ratio of NP diameter to the initial surface roughness of counterfaces. A representative model system is shown in Figure 5. Simulations were run for different NP sizes and initial surface roughness. The results show that, at low surface roughness, introducing small NPs into the system may decrease friction, while, at high surface roughness, any NPs may decrease friction, but a more significant effect is likely with larger NPs. It also indicates that, for a given surface roughness, there may be an optimal NP size for reducing friction. Analyses were also performed on the wear behavior of NPs, and, similarly, a correlation between NP size and initial surface roughness was identified. These results emphasize the importance of surface roughness and, in part, explains why the effect of NPs on tribological properties is so varied in literature, i.e., the initial surface roughness in testing was not consistent.

Conclusions

A series of oil-soluble hybrid NPs were synthesized by functionalizing NPs with oil-soluble ILs, organic ligands, and polymer brushes. These hybrid NPs can be dispersed in PAO, forming homogeneous dispersions that exhibited

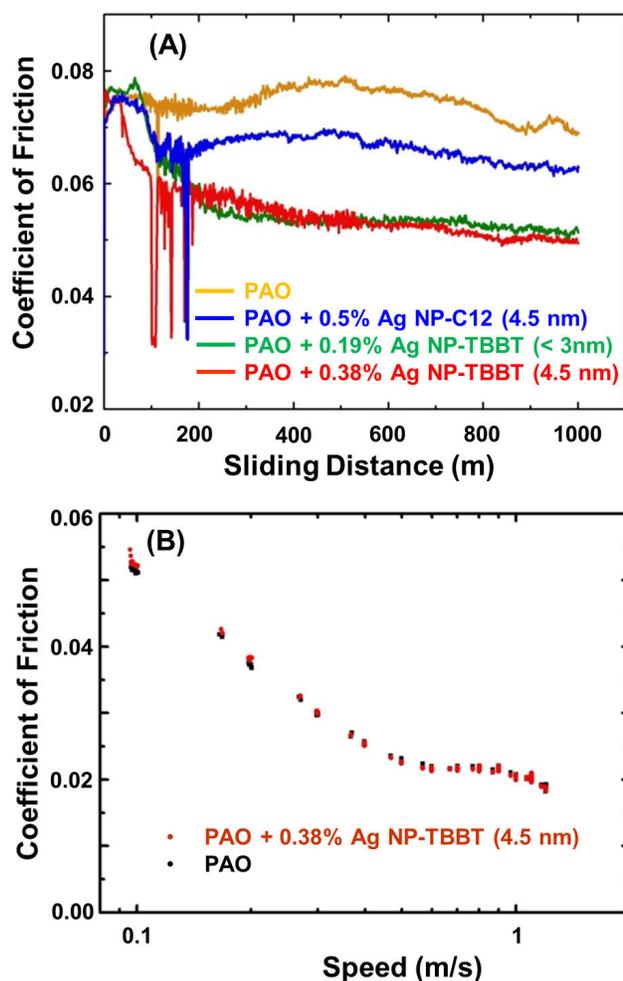


Figure 4. (A) Friction coefficient traces of PAO (orange), 4.5 nm Ag NP-C12 (blue), Ag NP-TBBT of <3 nm (green), and 4.5 nm Ag NP-TBBT (red). (B) Stribeck curves of neat PAO (black) and PAO containing 0.38 wt% Ag NP-TBBT of 4.5 nm (red).

excellent stability. Tribological bench tests showed ~50% friction reduction and ~80% wear reduction for IL-SiO₂NPs. Significant decreases in friction (up to ~40%) and wear (up to ~90%) were achieved with hairy NPs. Organic functionalized silver NPs demonstrated up to 35% of friction reduction and 80% wear reduction. These results indicate that hybrid NPs are promising engine lubricant additives for friction and wear reduction. Simulation study revealed the dependence of tribological effect of NPs on the ratio of NP size to the initial surface roughness of counter surfaces.

FY 2016 Publications/Presentations

1. Wright, R.A.E., Wang, K.W., Qu, J., Zhao, B. "Oil-Soluble Polymer Brush-Grafted Nanoparticles

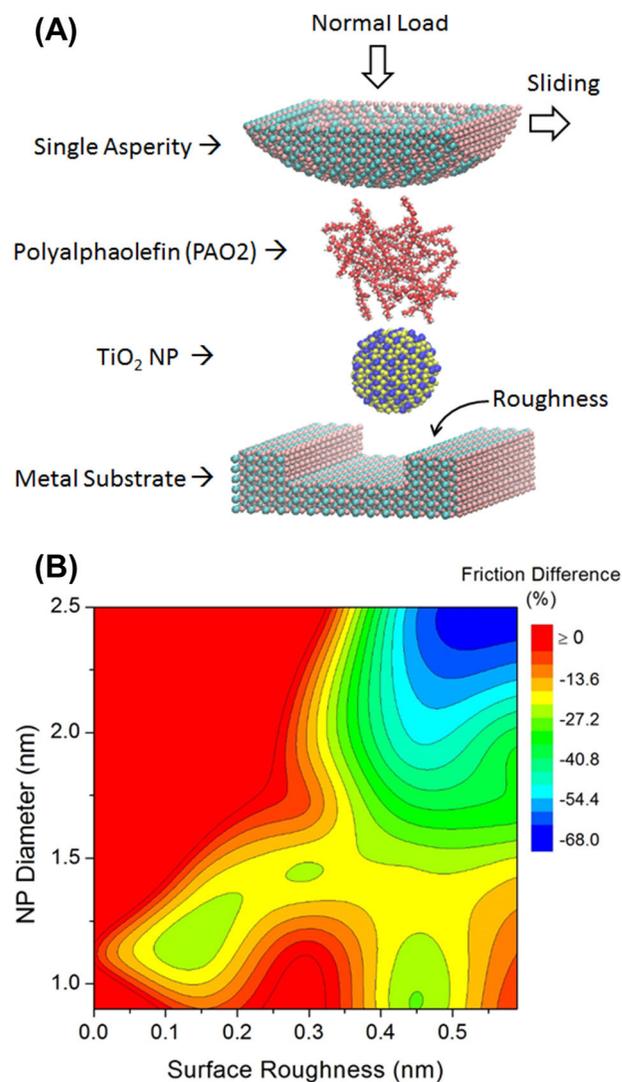


Figure 5. (A) Snapshot of molecular dynamics simulations of NP-additized PAO where the NP's size and the lower surface's initial roughness are varied. (B) Simulation results showing that NP size and counterface roughness have an interrelated effect on friction. Friction difference is the difference between the friction with and without NP, where a negative value indicates that NP lowers friction.

as Effective Lubricant Additives for Friction and Wear Reduction" *Angew. Chem. Int. Ed.* **2016**, *55*, 8656–8660.

2. Zhao, B. "Hybrid Ionic-Nano-Additives for Engine Lubrication to Improve Fuel Efficiency," DOE Annual Merit Review and Peer Evaluation Meeting in Washington, DC, June 6–10, 2016.
3. Zhao, B. "Hairy Nanoparticles," UT/VT workshop at University of Tennessee, Knoxville, Four Points Sheraton on April 18, 2016.

4. Martini, A. “Effect of Nanoparticle Size on the Tribological Properties of Nanolubricants,” STLE Annual Meeting, Las Vegas, NV (May 2016).
5. Gao, H. Student Poster: “Modeling the Effects of Nanoparticle Size and Surface Roughness on Friction in Boundary Lubrication,” STLE Annual Meeting, Las Vegas, NV (May 2016).

Special Recognition & Awards/ Patents Issued

1. Hongyu Gao – UC Merced Spring 2016 Graduate Dean’s Dissertation Fellowship.

V.4 Integrated Friction Reduction Technology to Improve Fuel Economy without Sacrificing Durability

Overall Objectives

- Develop GF-6A (backward compatible) 0W-20 fuel efficient lubricant formulation that is at least a 2% fuel economy improvement over a 5W-30 2014 GF-5 commercial oil (baseline) using the GF-6 specification engine sequence test available at the time of milestone due date; this can be used for the legacy fleet vehicles
- Develop 0W-16 GF-6B fuel efficient lubricant formulation that is at least a 2% fuel economy improvement over the baseline oil for 2018 or later engine models
- Develop test protocols to measure engine durability using the developed GF-6 oils, and evaluate the effectiveness of surface texture, diamond-like-carbon coating, and encapsulated additives in maintaining and/or enhancing durability in using GF-6 oils

Fiscal Year (FY) 2016 Objectives

- Bench test development to define the technical issues related to ultra-low viscosity lubricant development
- 0W-16 formulation development to achieve the maximum fuel efficiency possible while maintaining durability and stability using the latest additives from cooperative industrial partners
- Conduct ASTM Engine Sequence VIE to measure fuel economy improvement over the baseline oil (2014 5W-30 GF-5 commercial oil).
- Working with GM, fabricate various engine components with surface textures, carbon-based coatings, and chemical films in preparation for the upcoming durability testing to be conducted in FY 2017

FY 2016 Accomplishments

- We have conducted two repeat ASTM Engine Sequence VI-E tests on the 0W-20 formulation that was tested during the fourth quarter of FY 2015 to establish statistical confirmation of the engine test result of 2.39% fuel economy improvement (there was no national test statistics at the time on testing). The repeated tests confirm the results and affirm that the candidate oil has indeed exceeded the 2% fuel economy improvement over the 2014 baseline oil (5W-30 GF-5 certified oil). The prototype lubricant can be used by

Stephen Hsu (Primary Contact), Gefei Wu (Valvoline), Tim Cushing (General Motors)

George Washington University
323C Exploration Hall
20101 Academic Way
Ashburn, VA 20147
Phone: (571) 553-8365
Email: Stevehsu@gwu.edu

DOE Technology Development Manager:
Michael Weismiller

NETL Project Manager:
Adrienne Riggi

Subrecipients (cost share team partners):

- Ashland/Valvoline, Lexington, KY
- General Motors (GM), Detroit, MI

Additive company partners:

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

the legacy vehicles. This has the potential of saving 252,000,000 gallons of fuel per year.

- We have established cooperative arrangements with several additive companies to provide experimental or new concept friction modifiers and viscosity modifiers under a non-disclosure agreement. This arrangement allows us to develop formulations based on the latest additive technological concepts to achieve the state-of-the-art fuel efficient lubricants.
- Based on the newly available additive chemistries beyond current commercially available additives, we have developed advanced formulations that show superior performance potentials. The new additives, of course, will need formulation optimization and engine testing to confirm the benefits. The new formulation is now ready for engine testing. Unfortunately, the ASTM GF-6 specification tests, after a series of delays, were in the midst of engine test stand statistical matrix testing. Availability of the test matrix statistics will provide

validation without running repeat tests. We were not able to obtain an engine test stand during the fourth quarter of FY 2016. The oil has been blended and is currently waiting in line to be tested.

- The surface material technologies have been developed and being applied to the engine parts. This includes various surface textures and protective films. The engine parts will be used during the durability testing in FY 2017.

Future Directions

The GF-6 prototype oils will be shipped to GM as the baseline lubricants to conduct engine durability evaluation on the effect of low viscosity on engines. The tests will be designed and conducted by GM.

- The fuel economy improvement of the 0W-16 formulations will be measured in engines tests once the ASTM Sequence VI test stand is available.
- GM will design and conduct engine durability tests to measure the low viscosity oils and their effect on engine durability.
- The effects of the material technology will be tested in the engine performance tests to assess their effects. ■

Introduction

The demand for fuel to transport people and goods in the United States necessitates the need for oil import at about 9 Mbbbl/d. Improving the fuel economy of cars and light trucks therefore reduces dependence on foreign oil. The new Corporate Average Fuel Economy standard will raise fuel economy from 27.5 mpg in 2012 to 54.5 mpg by 2025. This project supports the national goal.

In 2012, the Japan Automobile Manufacturers Association petitioned SAE J300 to establish a new ultra-low viscosity grade of lubricants for enhanced fuel economy. SAE approved the new 0W-16 classification in 2014 (2.3 mPa.sec at 150°C). 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 a durability test protocol 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 and oxidative stability is

needed. While low viscosity reduces hydrodynamic drag and pumping energy, it still needs good friction modifiers, robust antiwear additives, and good high temperature viscosity index improvers to create robust fuel efficient lubricants.

To formulate a robust low viscosity lubricant, we have formed an alliance with additive companies, an oil company, and an engine manufacturer to create a vertically integrated team to develop advanced low viscosity lubricants and test them in engines. We have received over 130 individual additive components and base oils from the industrial partners. Together, we jointly develop state-of-the-art low viscosity lubricants, conduct engine tests to measure fuel economy improvements, and test for potential durability influence.

Results

Development of 0W-16 Formulations

This is the focus of FY 2016 program activities. It consists of four steps: (1) base oil selection, (2) friction modifiers research and testing, (3) antiwear additive selection and testing, and (4) formulation optimization. Several generations of formulations have been developed and tested and are waiting for engine testing.

The choice of low viscosity esters: While polyalphaolefin is the dominant low cost synthetic base oil, the low solvency of polyalphaolefin has to be compensated with ester base oil. We approached various ester base oil suppliers to provide oxidation-stable low viscosity complex esters. We were able to obtain eight ester base oils within the viscosity range for evaluation. Since low viscosity lubricants intrinsically may suffer from oxidative volatility, rapid vapor phase oxidation, and loss of lubricant under high temperature, the proper choice of the ester is important. The evaluation of the various oxidation related properties could be time consuming and difficult due to the complexity of the oxidation processes. We have developed a thermogravimetric analyzer test method to evaluate the oxidative volatility and deposit forming tendency. We measure the oil sample contained in an iron metal cup in Ar atmosphere to obtain the thermo-decomposition curve, and then we repeat the test in pure oxygen atmosphere. When the curves are superimposed as shown in Figure 1, we can measure the relative difference between thermo-decomposition and oxygen induced oxidation volatility weight loss. Quantitative results can be obtained by subtracting one curve from the other, yielding a difference curve. The areas under the curve provide indication with respect to oxidative volatility as well as deposit forming tendencies. Using this technique, we have evaluated eight low molecular weight ester base

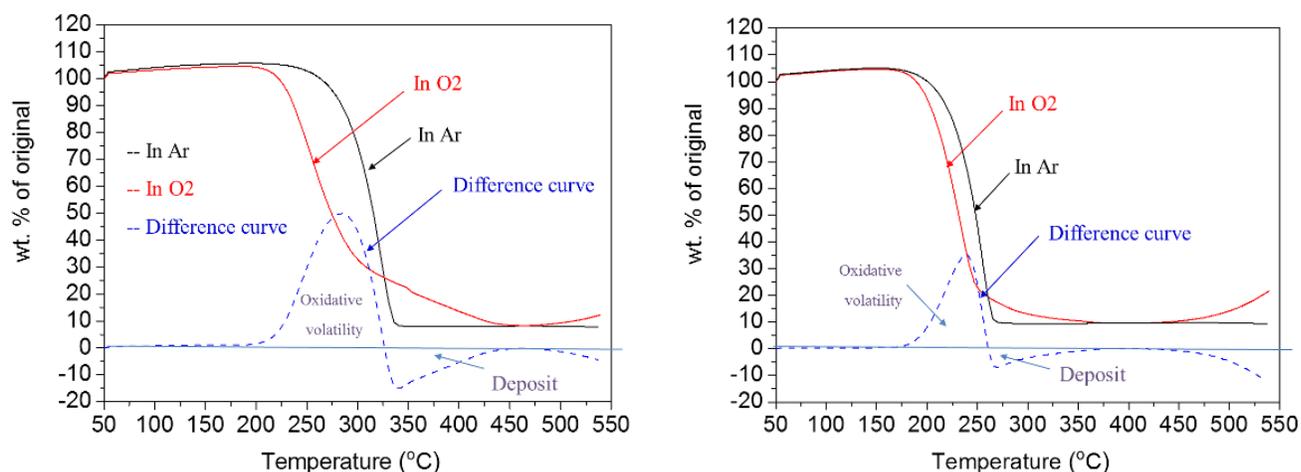


Figure 1. Difference curves of Ester 1 and Ester 2 showing different oxidative volatility and deposit forming tendency of the two esters shown

Table 1. Initial Candidate OW-16 Prototype Properties

	Baseline	Candidate Tested	New Candidate
	5W-30	OW-20	OW-16
KV100	10.67	8.675	6.9
KV40	62.02	36.038	28.2
VI	163	232	220
HTHS 150°C	3.13	2.64	2.27
Noack* (%)	14	11.5	13.38
CCS (cP)	6,013 (-30°C)	2,336 (-35°C)	1,946 (-35°C)
MRV (cP)	32,723 (-35°C)	6,546 (-40°C)	4,984 (-40°C)
Pour Point (°C)	-42	-60	-60
Gravity (g/mL)	0.8601	0.855	0.8536

*ASTM D-5800

HTHS - high temperature high shear; CCS - cold cranking simulator; MRV - mini-rotary viscometer; VI - viscosity index; KV100 - kinematic viscosity at 100°C; KV40 - kinematic viscosity at 40°C

oils to formulate the OW-16 oil. This is an important issue to develop an oxidative stable low viscosity lubricant that will maintain oil pressure during the engine operation.

With the base oils selected, working with Valvoline, a prototype OW-16 was formulated. Table 1 tabulates the resulting oil properties.

The oils were evaluated in the High Frequency Reciprocating Rig (HFRR) to measure friction and wear on standard steel samples at 125°C and 1.25 GPa contact pressure. Results are shown in Figure 2, comparing the three oils. The oils were also evaluated in the Mini

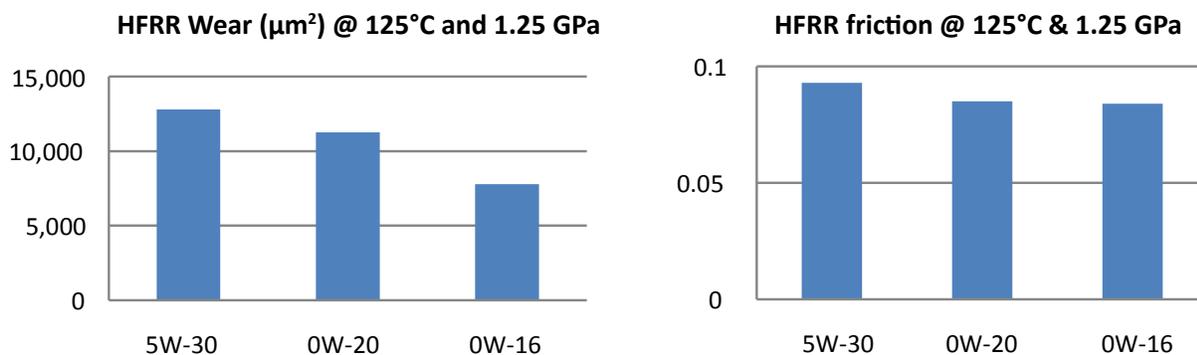


Figure 2. HFRR results of the three oils

Traction Machine (MTM) for frictional characteristics. Figure 3 shows the comparisons of the three oils.

Figure 2 shows that the new 0W-16 oil has a lower wear amount and comparable friction level, suggesting the formulation has improved friction and wear properties. Lower viscosity oils generally have higher friction and wear characteristics.

Figure 3 shows the Stribeck curves from the MTM test results. The areas under the curves suggest that the difference between 5W-30 and 0W-20 is larger than the difference between 0W-20 to 0W-16. Therefore, the improvement in fuel economy shifting from 0W-20 to 0W-16 may not be that large. Indeed, some engine tests reports in the literature tend to confirm this observation.

Search for new friction modifiers: Miller [1] and Ushioda [2] studied the effect of low viscosity oils on fuel economy using a motored engine torque test 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 significantly in order to gain fuel economy further.

Based on their data, we began to search for better friction modifiers and test them in our prototype formulations. After several rounds of testing, most of the current available friction modifiers were tested with

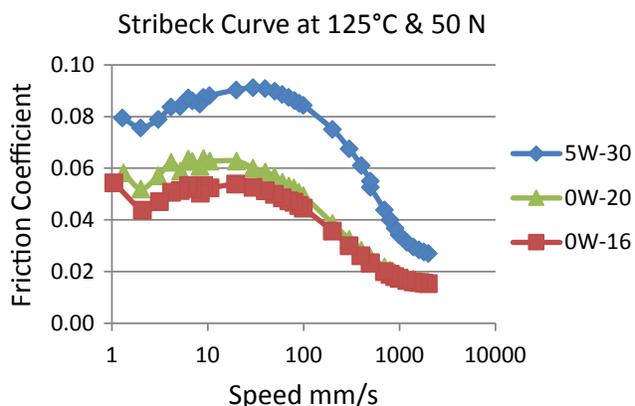
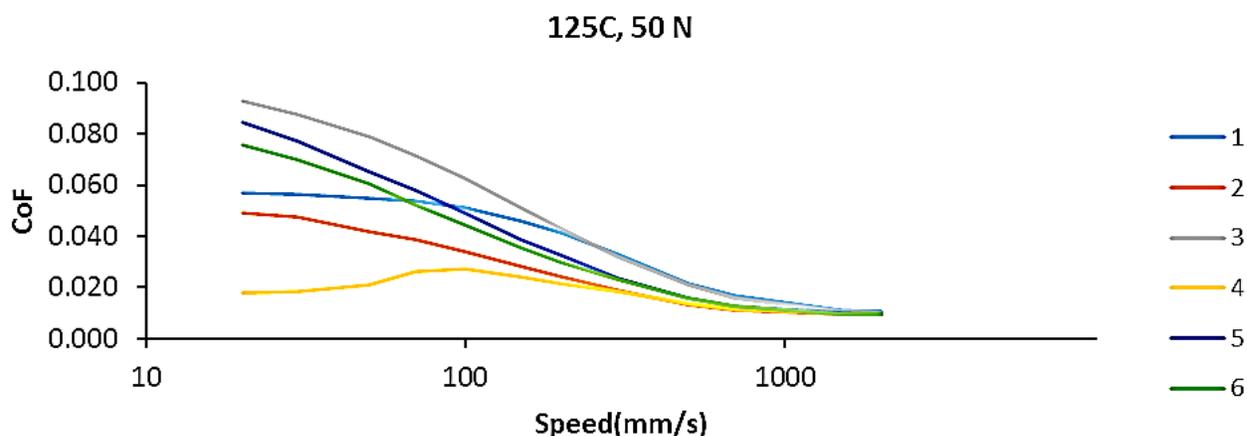


Figure 3. MTM test results of the prototype 0W-16 formulation showing the difference in frictional behavior of the three oils

the combination of Moly-containing additive together with functionalized organic friction modifiers exhibit consistent higher performance but not sufficient to change the predicted fuel economy improvement analysis as shown in Figure 3.

We discussed our finding with several additive suppliers. One company offered an experimental viscosity modifier–friction modifier additive to us for testing under a non-disclosure agreement. The MTM test results of this new viscosity modifier–friction modifier are shown in Figure 4.

Figure 4 shows the data of several friction modifiers. The top three curves represent conventional friction modifiers that we have tested. The bottom three curves are obtained by using this new friction modifier family. The figure shows that this family of friction modifiers has outstanding friction reduction (in this formulation) to reduce friction under elasto-hydrodynamic lubrication and boundary lubrication regions of the MTM test protocol. This is a



CoF - coefficient of friction

Figure 4. New friction modifier evaluation using the MTM at 125°C, 50% roll-slide ratio, 50 N load, and increasing speeds

major breakthrough. Subsequently the company informed us that they were commercializing this family of additives.

Evaluation of antiwear additives: Since antiwear additives have the potential to interact with friction modifiers, the test protocols call for screening antiwear additives in a formulation with a fixed friction modifier. The best antiwear additive selected from the screening then go through another round of screening where the antiwear additive is fixed and various friction modifiers are inserted. The new friction modifier went through this process and they were validated.

Evaluation of viscosity modifiers: New viscosity modifiers are also evaluated. We have collected traditional viscosity modifiers (also called viscosity index improver) as well as a new generation of viscosity modifiers such as star molecules and functionalized viscosity modifiers. The ability of these molecules to bolster viscosity at high temperature, hence higher oil film thickness, is also an effective way to formulate ultralow viscosity lubricants to lower friction and prevent wear.

Summary: Taking the results of all the evaluations and optimize the formulations several times, we finally arrive at the final two versions of 0W-16 formulations.

Engine Testing

The GF-6 specification engine tests are new tests that need to be developed. The process began in 2012 and was scheduled to be completed by 2016. However, GF-6 specifications is a leap of technology, unlike the normal progression of GF specifications. Many technical difficulties were encountered and caused consecutive delays. The completion of the test specification is now expected in the fall of 2018 for the ASTM Engine

Sequence VIE test, the official definitive fuel economy measurement test. In June 2016, ASTM found that a variant of the Sequence VIE test has to be set up to measure 0W-16 oils. The modified test procedure was named VIF. The newly created test procedure will need to follow the normal test procedure development protocol and finding a set of reference oils, test stand reference oils, and carry out statistical matrix testing. This was unanticipated and was a surprise to the industry. The engine test stand we originally scheduled to conduct the Sequence VIF test was fully occupied and unavailable to us. So our engine validation of the fuel economy gains will have to wait until the engine test stand becomes available.

However, based on the bench test results, we project our 0W-16 formulation will gain about 3.1%, which we will verify with engine test results.

Microencapsulated Additive

We have successfully completed the development of microencapsulation of lubricant additives in 2016. Depending on the specific additive chemical structure, we have to design the process, using specific emulsifier, reaction conditions, and control the size of the capsules and the capsule wall thickness. The process for each additive is different. There appears to be no universal process that will work for all additives.

Microcapsules containing a single additive component when synthesized, the polymer chemistry, and the reaction conditions control the release mechanism of the additive inside the capsules. Literature reported many chemical methods that will preferentially provide triggers to induce the breaking up of the capsules and release the content. In automobile lubricant applications, most of these methods

do not apply since they are related to much structurally weaker capsule polymer chemistry, such as membranes to encapsulate chemicals. The automobile lubricant environment in an operating engine is so severe that only high melting shear-stable capsules could survive.

After making the capsules to be survivable in an engine environment, there are very limited time release mechanisms that can be used. The most useful ones are those release mechanisms based on temperature, shear stress, and acidity of the solution environment. In making capsules, we have adopted a three-step procedure to ensure quality and self-consistency: (1) encapsulate the intended additive, (2) break the capsule manually and recover the additive, and (3) compare the recovered additive with virgin additive to ensure the functionality remains the same. In testing the capsules after these three steps, we also would compare virgin additive at a dosage with the capsules added at the same dosage rate that our recovery study revealed. These steps are important to avoid accidental or unrepeatable results.

Since the most important additive in this project is friction modifiers, we will choose the friction modifier capsule to illustrate the procedure that we used. Figure 5 shows the results of the encapsulated friction modifier tested in a ring and liner tester (Plint TE77) using a production ring segment sliding against a production liner segment with cross-hatched surface. The test was conducted at 100°C with reciprocating motion at a speed of 24 Hz, step-loading from 30 N to 240 N with a step interval of 6 min each.

As can be seen in Figure 5, the oil containing 1.5% friction modifier shows steady friction reduction dramatically from the baseline case. The baseline case friction rises with increased loading approaching a friction coefficient of 0.08 while the oil with 1.5% friction modifier shows around 0.036 after initial steady state friction, then drops to 0.02 even as the load is increasing. The oil containing the same friction modifier at 1.5% equivalent amount in capsulated form shows an initial coefficient of friction of about 0.04, then rises slightly to 0.042, then continually decreases as the load increases. This is probably due to gradual release of the friction modifier through the temperature and shear trigger mechanisms.

We have now shown that capsulated friction modifier reduces friction and is equivalent to virgin friction modifier, the question then is how to show time release capability of the capsulated friction modifiers? In real engine operation, the capsules would exist in the oil but not function in full dosage. The oil would have to carry

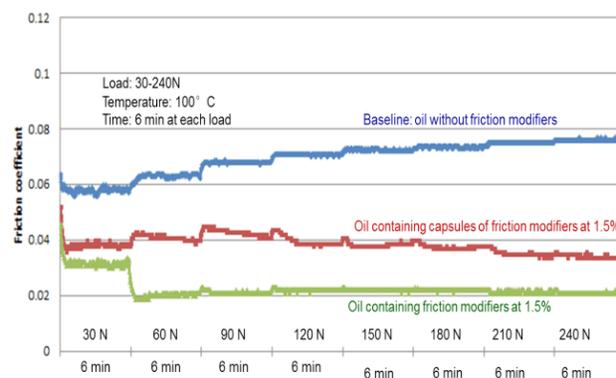


Figure 5. Comparison of encapsulated friction modifier performance among the baseline case that does not contain any friction modifier additive with oil containing 1.5% friction modifier and oil containing 1.5% equivalent friction modifier capsules

the normal treat rate of friction modifier in order to reduce the friction. Therefore, if we design an experiment to simulate the engine conditions to cause the lubricant to degrade, the normal treat rate of friction modifier would be oxidized and degraded with the additives in the lubricant. Then if the capsules begin to release the friction modifiers, the friction level would maintain the low friction without going up as the additives become depleted.

Based on this strategy, we designed an oxidation–friction test to test the time release property of the capsulated friction modifier. The oxidation test was conducted at 170°C with 20 cc air bubbling through the oil using a small 3-mm diameter capillary glass tube. The oil volume was 125 cc with 1 wt% iron naphthenate and 1 wt% copper naphthenate as catalysts. The oil used was the GF-6A 0W-20 lubricant tested in this program. Periodic samples of 2 cc oxidized oil were withdrawn for viscosity measurements and the friction measurement. The friction measurements were conducted using a four-ball wear tester in ball on three flats configuration. The three flats were made of 52100 through hardened steel, and wear scars were created on the flats using a 30 min wear test under 40 kg load, 600 rpm, at 80°C. The 2 cc sample was sufficient to cover the three flats for friction testing.

As shown in Figure 6, the baseline oil (containing friction modifier in the formulation) friction begins to rise as the oxidation proceeds under the oxidation condition, indicating additive depletion. Oils that contain additional friction modifier capsules at 0.5%, 1%, 1.5%, and 2% levels show decreasing friction as a function of capsule concentrations. This suggests that the capsules were able to release the friction modifier to maintain the same level

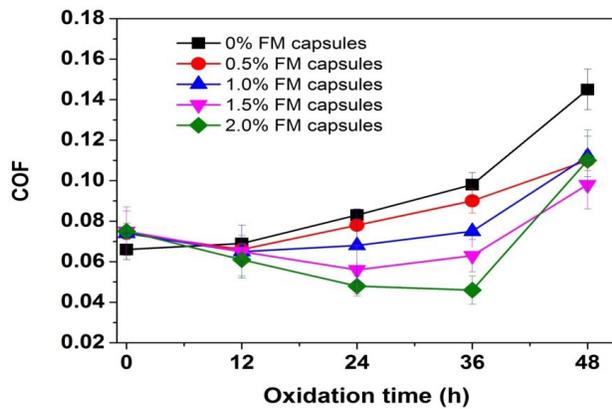


Figure 6. Friction measurement of various concentrations of capsulated friction modifier (FM) vs. baseline that does not have any friction modifier capsules but was fully formulated

of friction at 1% level and even decrease the friction level when additional capsules were available. This clearly demonstrates that the microencapsulated friction modifier was able to release the additive as a function of time, fulfilling the requirement.

We have completed all milestones related to microencapsulation. Details can be found in the quarterly reports of this project.

Surface Material Technology

For FY 2016, we have been busy preparing test samples and developing surface texture fabrication technology to put computer generated pattern onto the engine component surfaces. Associated with the surface texture fabrication and designs, we also explore the deposition of diamond-like carbon coatings, graphene thin films, and bonded chemical films that are reactive towards carbon. The materials technologies were evaluated by bench tests. The most challenging task is to reduce cost and simplify the surface texturing fabrication process. We have been using the National Institute of Standards and Technology NanoFab facility in Gaithersburg, Maryland, to develop a direct write soft in-hole mask technology to skip the normal micro photolithography ultraviolet exposure step

on engine components. We use the new soft mask facility that the National Institute of Standards and Technology NanoFab has installed one year ago to facilitate such undertaking. We have succeeded in developing this through-hole soft mask technology.

Conclusions

We have successfully met the milestone in developing GF-6B oil, currently awaiting engine test validation. According to our modeling, it will exceed the 2% fuel economy improvement. This oil is intended to be used in new engine models, produced in 2018 or later.

References

1. 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.
2. 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 2016 Publications/Presentations

1. "New generation of low viscosity fuel efficient lubricants: key technical issues," S. Hsu, F. Zhao, Plenary Lecture, Tribology in Industry and Research Symposium, Wiener Neustadt, Austria, November 25, 2015.
2. "Microencapsulation of additives," F. Zhao, S. Hsu, STLE Annual Conference, Dallas Texas, May 17–21, 2016.
3. "Low viscosity fuel efficient lubricants: key technical issues," Fei Zhao, S. Hsu, STLE Annual Meeting, May 15–19, Las Vegas, Nevada, 2016.
4. "Microencapsulation of friction modifiers," Fei Zhao, Sulaksha Parab, S. Hsu, STLE Annual Meeting, May 15–19, Las Vegas, Nevada, 2016.

V.5 A Novel Lubricant Formulation Scheme for 2% Fuel Efficiency Improvement

Overall Objectives

NU is developing novel lubricant formulations for improving vehicle fuel efficiency by at least 2% without adversely impacting vehicle performance or durability.

Fiscal Year (FY) 2016 Objectives

- Further improvement of the heterocyclic friction modifiers (FMs) for boundary lubrication (BL)
- Design and synthesis of diblock copolymer viscosity modifiers (VMs) for low shear at high speeds
- Molecular dynamics (MD) modeling of the FMs and VMs, and surface physical and chemical investigations
- 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

FY 2016 Accomplishments

- Synthesized and characterized three major families of heterocyclic FMs, whose BL performances were also optimized greatly
- Designed and conducted the synthesis of the first generations of copolymers as VMs
- 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
- Investigated entanglement and alignment of FM molecules in their surface adsorption and VMs' shear-thinning transition via MD simulations
- Conducted ultra-thin film measurements and verified the reinforcement of the lubricant film in the BL regime
- Better understood the origins of the significantly improved BL performances by means of microscale nanoscratch experiments and thermodynamic analyses
- Trained postdoctoral researchers, graduate, and undergraduate students; three graduated, one with a Masters of Science and two (partially involved) with doctorates

**Q. Jane Wang (Primary Contact),
Y.W. Chung, T.J. Marks, T.L. Lohr,
M. Desanker, X. He**

Northwestern University (NU)
2145 Sheridan Road
Evanston, IL 60208
Phone: (847) 467-7510
Email: qwang@northwestern.edu

Ali Erdemir and Aaron Greco

Argonne National Laboratory (ANL)
9700 S. Cass Avenue
Argonne, IL 60439

DOE Technology Development Manager:
Michael Weismiller

NETL Project Manager:
Carl Maronde

Future Directions

- Further improvements of heterocyclic FMs, copolymer VMs, and functionalized NPs
- More laboratory tests considering more comprehensive conditions, oil aeration effects, and oxidation stability
- Developments of lubricant formulations and industrial verification tests ■

Introduction

Achieving more than 2% fuel efficiency improvement of light- and medium-duty vehicles requires significant friction reduction in the powertrain and drivetrain systems; if by reducing boundary friction alone, this requires at least a 30% friction reduction [1]. Better FMs are needed as a component to achieve this BL goal. The frictional loss due to high viscous shear at high speeds cannot be simply tackled by using oil of low viscosity because this will raise the friction at low speeds. We need a chemically and mechanically stable 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 rate 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 NP-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 NU–ANL team, supported by collaborative industries. All additives were synthesized or prepared at NU’s chemistry laboratory and tested at the tribology laboratories at NU and ANL.

Results

Entanglement and Alignment of FM Molecules During Surface Adsorption

Time and temperature influence the surface adsorption processes. MD simulations were conducted to further study the FMs at both the beginning stage and the final stage. At the initial stage, the FM molecules were randomly distributed in the space just above the hydrated surface (random model), and they approached the surface from all possible directions. An aligned model was designed for the last stage aiming at capturing the well-adsorbed FM molecules in favorable orientations. Interaction energies of the adsorbed C18Cyc molecules in these two different models show a larger difference (Figure 1a), suggesting that an obviously higher energy should be input into the system to overcome the energy barrier between the initial stage and the final stage for a spontaneous realignment. However, adsorption of C18amine molecules demonstrates a very small difference of the interaction energies between the random and aligned models (Figure 1b). During their adsorption, the C18amine system requires a small energy input from the environment, and the realignment of C18amine molecules can take place spontaneously given enough

time. The temperature effects were then considered in the simulations to study the desorption possibility. The interaction energies of both FMs under alignment decrease at elevated temperatures, but a desorption process appears for the amine FM molecules only. The average mass center of the C18Cyc molecules arises by less than 5% due to expanded bond lengths up on heating, but no obvious desorption was found for them at high temperatures (Figure 1c). On the contrary, fewer and fewer C18amine molecules simulated stay on the surface at higher temperatures (Figure 1d), and only about one half of them remain being adsorbed at 200°C.

The adsorption and alignment of FM molecules could also be uncovered by the nanoscratch experiments at the microscale. Real-time adhesion–friction results of different adsorbed FM layers on silicon surfaces are shown in Figures 2a and 2b. Right after the dip-coating, the adsorbed C18Cyc layers reduce friction just slightly more than do the commercial FM (Armeen T) layers (Figure 2a). Toluene is a common organic solvent and was used to rinse the coated surfaces, after which the adsorbed C18Cyc molecular layers still reduce friction by about 70% at least (see the green plots in Figure 2b), indicating that the heterocyclic molecules could be strongly adsorbed on the surface and cannot be removed by the organic solvent. The surface adsorption is a kinetic process, and such significant adhesion friction reduction well maintains with the dip-coating duration. On the contrary, the weakly bonded commercial amine (Armeen T) molecules could be washed away completely by the solvent, and the nanoscratch processes show no reduction of the adhesive friction (see the red plots in Figure 2b). In addition, corresponding surface topography was also inspected by the atomic force microscopy (AFM) phase mapping, which showed a clear material removal process for the Armeen T coating but a visible inhomogeneity for the cyclen FM-coated surface. Entanglement and alignment of FM molecules during the surface adsorption is a time and temperature dependent process. These results from the microscale tribo-tests and characterizations are found to be well in accord with those from the MD simulations, and they address an important cause for the greatly improved BL performances.

Dependence of adsorption and desorption on temperature has also been evaluated to better understand the enhanced BL films in our previous elastohydrodynamic lubrication test results. From a thermodynamic point of view, the temperature activated alignment/interaction of the heterocyclic FM molecules is a critical supportive evidence to these unique, optimized surface adsorption and BL film enhancement mechanisms.

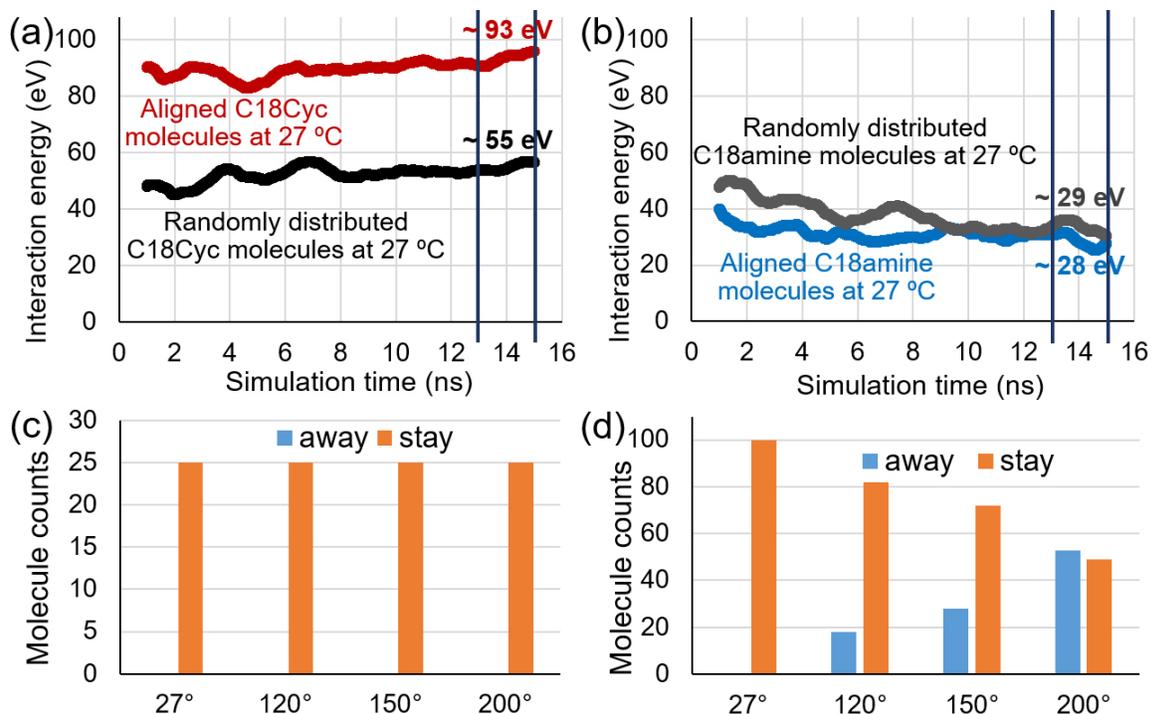


Figure 1. Interaction energy of C18Cyc molecules (a) and C18amine molecules (b) versus simulation time; average values of the interaction energies in the last 2 ns are labeled in the figures. Counts of the adsorbed C18Cyc molecules (c) and the adsorbed C18amine molecules (d) at elevated temperatures.

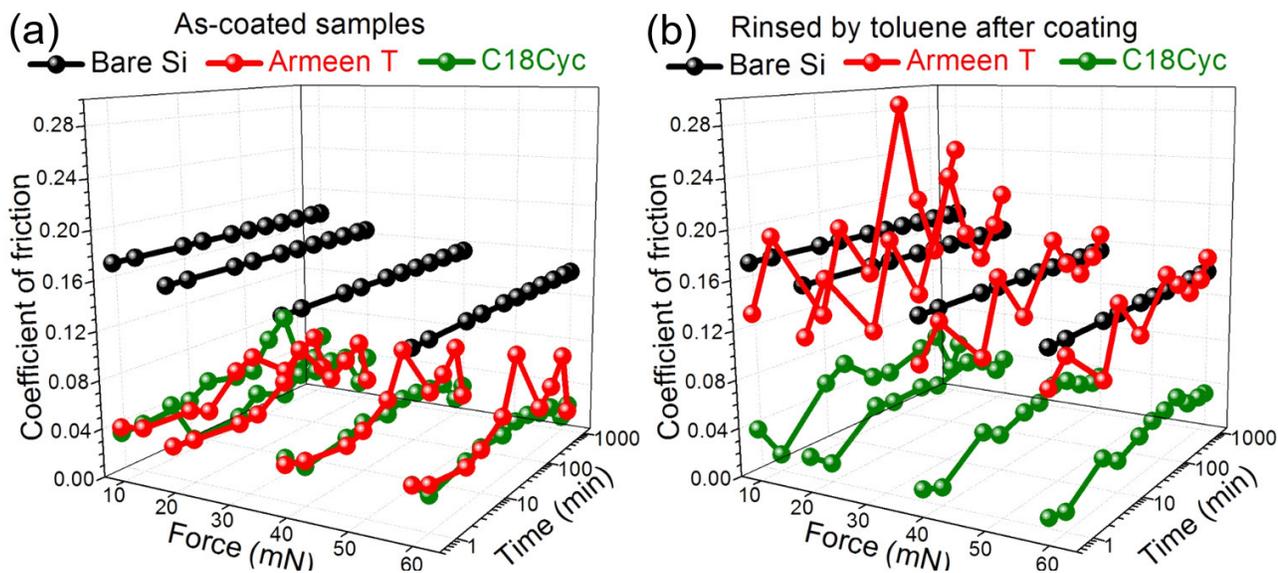


Figure 2. (a) Nanoscratch test results of dip-coated layers on Si surfaces before (a) and after (b) rinse with toluene. The coatings are processed in different durations.

Extended High-Temperature Pretreatment of Cyclen FMs for Further Enhanced Performances

Cyclen derivatives have been proven to be the most effective FMs tested so far. However, the oil solubility at room temperature became worse when the side hydrocarbon length increases from 12 carbons (C12Cyc) to 18 carbons (C18Cyc). An extended high-temperature pretreatment was designed to make C18Cyc more soluble in base oils. The nuclear magnetic resonance (NMR) and thermogravimetric analyses showed no structural changes for these molecules. Tribological results obtained from the pin-on-disk tests at 25°C to 200°C are shown in Figure 3. C18Cyc shows a better friction reduction than C12Cyc after the high temperature pretreatment. A continuous friction reduction throughout the temperature range tested is obtained for the C18Cyc at both speeds tested. Specifically, its percentages of friction reduction at 1.5 mm/s and 15 mm/s increase respectively from ~35% to ~65% and from ~25% to ~40% up on heating (Figure 3). Such significant BL friction reductions are much more than those brought by the commercial amine (ArmeenT) to the same base oil. Increased oil solubility of C18Cyc may lead to efficient surface adsorption and intermolecular entanglements, which were found to be essential for the significant lubrication improvement in BL regimes. An even longer pretreatment (125 h long) was also conducted to study the durability of the cyclen FM in the lubricants, from which no deterioration of the anti-friction performances was found for the C18Cyc. The new heterocyclic additive could be a very promising FM candidate due to its beneficial friction reduction

in BL regime, improved solubility, and extended high-temperature stability and durability.

Design and Synthesis of Diblock Copolymer-Based VMs

Our previous work on synthesizing diblock copolymer VMs yielded very low amounts of polymer products. We are working on increasing the yield of the polymerization.

Approach 1: Palladium Catalyst – Group 10 polymerization catalysts (Ni, Pd) have been shown to be less oxophilic, and as a result, more tolerant of polar comonomers. Pd catalysts have been shown to randomly copolymerize ethylene and methyl acrylates. Another advantage is that these catalysts form highly branched polyethylene (PE), which could be explored as a candidate VM. Although Pd catalysts can tolerate polar monomers, they are incapable of homopolymerizing polar monomers. Therefore it will be challenging to achieve the diblock copolymer structure we were initially aiming for.

Approach 2: Organolanthanide Catalyst – Organolanthanides are capable of homopolymerizing ethylene and methyl acrylate. Since this catalyst is tolerant of ethylene and polar monomers, we are able to make block copolymers fairly simply. A drawback of organolanthanide catalysts is that they form linear polymer only. The PE block produced with this catalyst is completely linear. This linear polyethylene has very poor solubility in base oil. Larger α -olefins are needed to improve the solubility, which the majority of organolanthanide catalysts are unable to tolerate due to the increased steric hindrance. The organolanthanide

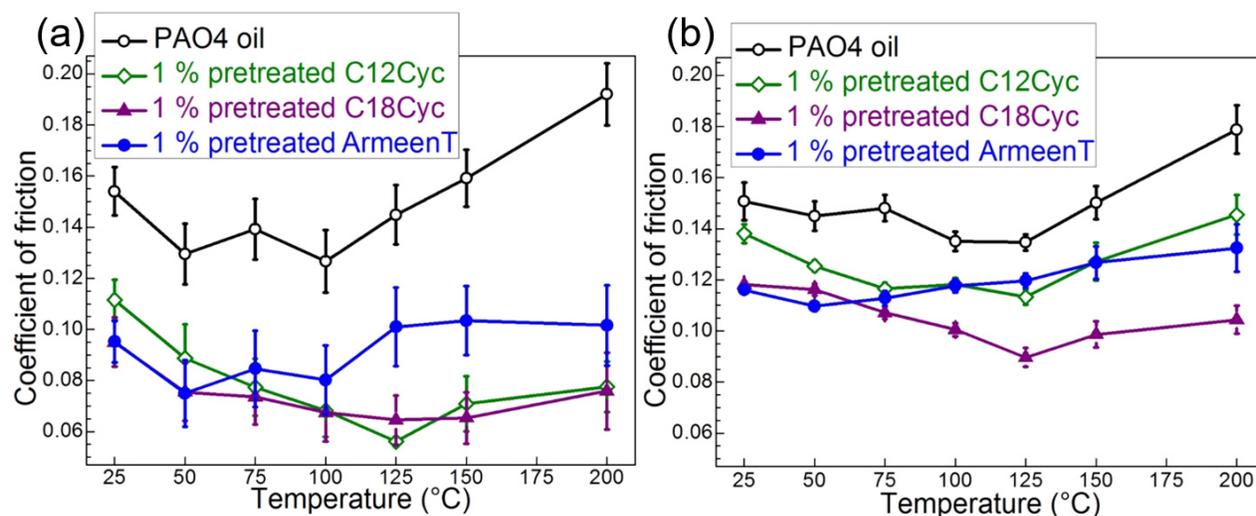


Figure 3. High temperature BL test results at 1.5 mm/s (a) and 15 mm/s (b) for PAO4 oil with and without addition of 1 wt% different FMs; all oils were pretreated at 120°C for 24 h.

catalysts have not yet been shown to make more oil-soluble hyperbranched polymers. Therefore, it is difficult to produce viable diblock copolymers using the organolanthanide catalysis.

Approach 3: Metallocene Catalysis and Atom Transfer Radical Polymerization (ATRP) – The polymerization termination mechanism that is most common with this catalyst is β -hydrogen elimination, which generates a terminal double bond on the branched polymer block. This double bond can then be used as a reactive site to impart terminal functionality onto the polymer. By turning this double bond into a radical initiator, we can then use this as a starting point for the synthesis of the coiled polymer block. Most recently, new reactions were adopted to convert the branched polymer block to a halogen-terminated branched block. NMR peaks corresponding to the double bond on the end of the branched polymer molecule disappear (Figure 4a). The halogen-terminated branched polymer block was used in a test reaction as an initiator for ATRP (Figure 4b). Proton NMR of the product has peaks corresponding to both branched polymer block and coiled polymer block, which is a good indicator that we have the diblock copolymer. Gel permeation chromatography results will be reported in the future to tell if this is the result of a single polymer consisting of both blocks or a mixture of two separate polymer blocks.

Lubrication Performances of the Randomly Branched PE as a VM

Polymerization yields have increased greatly since the new Pd catalyst was introduced to the synthesis. This partially synthesized VM (number average molecular weight = 141.8 KDa, polydispersity index = 1.62) possesses a randomly distributed branched polymer block only. An effective thermo-thickening behavior was demonstrated by using less randomly branched PE in the PAO4 base oil. Viscosity index improvement of the base oil was tested to be 140% at least with the addition of 8 wt% randomly branched PE. An improved shearing performance by this branched polymer block was also found in our rheological studies. With the better thermo-thickening and shear thinning properties, the enhanced high-temperature lubrication properties of the new VM are shown in Figures 5a and 5b. The tribological tests shown here started from hydrodynamic lubrications at room temperature and turned into mixed lubrications or boundary lubrications at high temperatures. Comparing to the commercial olefin copolymer (OCP) VM, more friction reduction are found by the newly synthesized PE VM at the both of the speeds tested. When the sliding speed is relatively low (150 mm/s, Figure 5a), the shear-thinning performance dominates the lubrication process at beginning, which is taken over later by the boundary lubrication or mixed lubrication process after the oil film comes to a rupture up on heating. The PE VM reduces

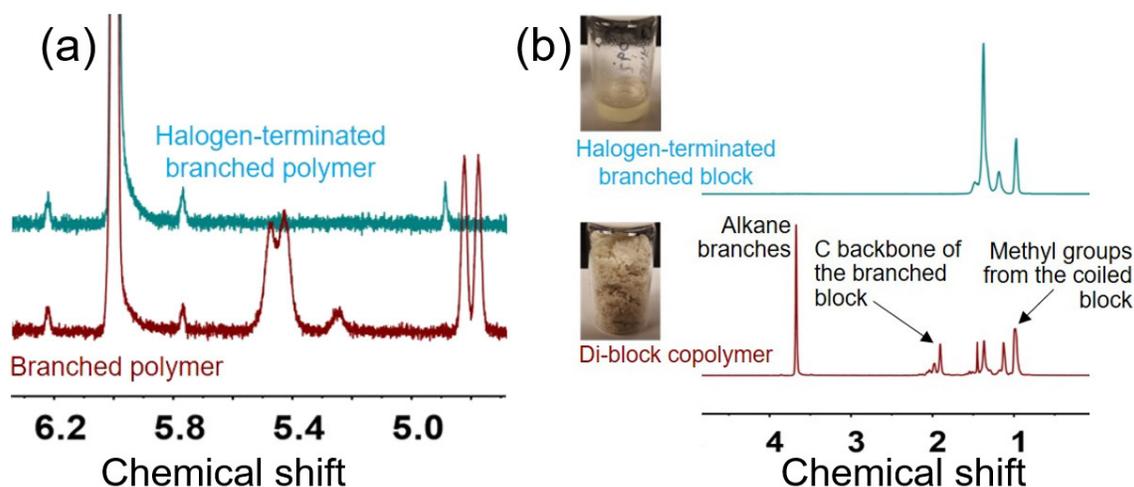


Figure 4. (a) Proton NMR spectra for branched polymer (bottom) and halogen-terminated branched polymer (top). (b) Proton NMR of halogen-terminated branched polymer (top) and (proposed) diblock copolymer (bottom); inset images show the visual difference between the two polymers.

~20% more friction than the commercial OCP VM before entering mixed or boundary lubrication at this speed. For the relatively high speed tests (500 mm/s, Figure 5b), the shear-thinning performance of the thermo-thickening VM is improved at the elevated temperatures. About 15% more lubrication improvement is obtained at this high speed from the PE VM than that from the OCP VM in PAO4 oil. The randomly branched PE has been proven to possess a better shear thinning property and an enhanced viscosity-temperature stability. It will be a suitable branch block for finalizing the diblock VM synthesis.

Evaluations of a Preliminary Lubricant Formulation Based on the Cyclen FM and the Randomly Branched PE

FMs should be capable of reducing friction further in the high-temperature, high-speed tests shown in Figure 5. A preliminary lubricant formulation is then prepared

by mixing our best candidate FM (C18Cyc) with the randomly branched PE VM in a PAO4 oil. C18Cyc FM makes the PE VM mixture work better, especially for the high temperature tests in boundary or mixed lubrication (Figures 5c and 5d). Just the heterocyclic FM in PAO4 can reduce even more friction than the FM in the preliminary FM/VM lubricant formulation. As far as the friction tests are concerned in the BL regimes, the novel cyclen FM could well maintain its exceptional friction reduction capability no matter the sliding speeds are low or high. A fully formulated synthetic 5W-30 engine oil (Mobil 1™ silver) was also tested as an up-to-date control sample. It only shows better high-speed lubrication performances than does the base oil. All the lubricant additives and the formulation developed at the current stage of research have exhibited noticeable improvements over this commercially available motor oil.

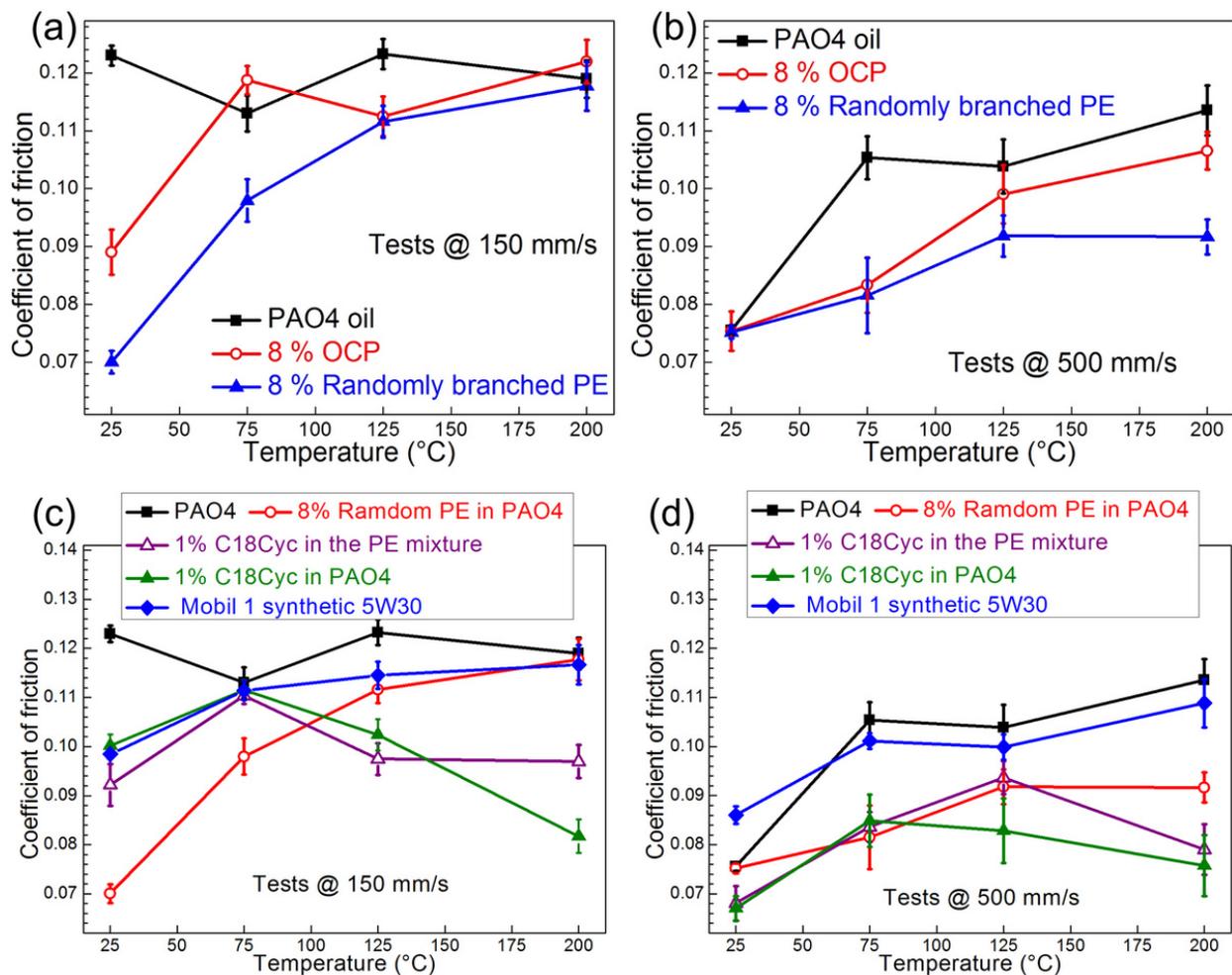


Figure 5. High-temperature lubrication tests at 150 mm/s (a) and 500 mm/s (b) in PAO4 oils with or without different VMs. High-temperature lubrication tests of the preliminary FM/VM formulation with selected references at 150 mm/s (c) and 500 mm/s (d).

Conclusions

- Entanglement and alignment of the FM molecules in their surface adsorptions investigated by MD simulations, real-time nanoscratch tests, and AFM phase mapping, are believed to be a functional difference between our novel FMs and the conventional alkane-based FMs.
- Dependence of the BL film on adsorption and desorption thermodynamics is analyzed for more in-depth understanding of the excellent tribological performances.
- BL performances of the cyclen derivatives improved further by an extended high-temperature pretreatment, which leads to beneficial stability, durability, and BL friction reduction confirmed for the new heterocyclic FMs.
- Surface adsorption and BL film reinforcement has proven to be the principal mechanisms for BL improvement; the novel heterocyclic FMs are capable of performing both roles better.
- Group 10, organolanthanide, and metallocene polymerization catalysts were evaluated thoroughly in synthesizing the diblock copolymer VMs with appreciable yields; ATRP with a metallocene catalysis process was found to be the most suitable approach.
- Both tribological and rheological improvements by the randomly-branched PE VM identified, indicating that this molecule is a suitable branch block for finalizing the diblock VM synthesis.
- Lubrication performances of a preliminary FM/VM formulation were evaluated in a wide temperature range; more tribological improvements were confirmed for the new additives or the lubricant formulation developed in the present research.

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 conjunctions," *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).

FY 2016 Publications/Presentations

1. M. Desanker, X. He, J. Lu, P. Liu, D. Pickens, Z. Liu, M. Delferro, T.J. Marks, Y.-W. Chung, Q.J. Wang, Alkyl-Cyclens as Effective Sulphur- and Phosphorus-Free Friction Modifiers for Boundary Lubrication, submitted, 2016.
2. T. Zolper, Y. He, M. Delferro, P. Shiller, G. Doll, B. LotfizadehDehkordi, N. Ren, F. Lockwood, T.J. Marks, Y.-W. Chung, A. Greco, A. Erdemir, Q. J. Wang, Investigation of Shear-Thinning Behavior on Film Thickness and Friction Coefficient of Polyalphaolefin Base Fluids with Varying Olefin Copolymer Content, *J. Tribol.*, 2016, 139, 021504.
3. He, X., Desanker, M., Lu, J., Pickens, D., Lohr, T., Delferro, M., Ren, N., Lockwood, F. E., Chung, Y.W., Marks, T.J., Wang, Q., "Characterization of Boundary Lubrication Film Formed by Alkyl-Cyclen Friction Modifiers," 71st STLE Annual Meeting, Las Vegas, NV, May 2016.
4. Lu, J., He, X., Desanker, M., Liu, P., Delferro, M., Chung, Y.W., Marks, T.J., Wang, Q., "Entanglement and Self-alignment of Heterocyclic Friction Modifier Molecules during Surface Adsorption: from MD Simulation to Experiments," 71st STLE Annual Meeting, Las Vegas, NV, May 2016.
5. Lu, J., He, X., Liu, P., Ren, N., Delferro, M., Chung, Y.W., Marks, T.J., Wang, Q., "Approaching the Rheological Properties of Base oil with Viscosity Modifier by Molecular Dynamics Simulations," 71st STLE Annual Meeting, Las Vegas, NV, May 2016.
6. Another four journal papers are under preparation.

Special Recognitions & Awards/ Patents Issued

1. Blake Johnson, Michael Desanker, Jie Lu, and David Pickens, First Place Winners, BASF Science Competition, 2016.
2. Wang, Q., International Award, STLE, 2015.

3. Marks, T.J., Luigi Sacconi Medal, Italian Chemical Society, 2015.
4. Marks, T.J., Derek Birchall Award, Royal Society of Chemistry, 2015
5. Delferro, M., Chung, Y.W., Marks, T.J., Wang, Q., Densanker, M., He, X., “Cyclen friction modifiers for boundary lubrication.” U.S. Patent, PCT/US2016/031868, May 2016.
6. Another patent based on triazine compounds is under preparation.

V.6 Improve 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 – greater than 2% by SAE J1321
- Durability penalty – none, no detriment seen in component life at 2,000 h tear down

Fiscal Year (FY) 2016 Objectives

- Reformulate the two engine oil candidates per the learning from the Cummins ISL 8.9 L engine installed at NREL from the engine fuel efficiency (FE) verification tests
- Rerun the ISL 8.9 L FE engine test at NREL on two engine oil candidates; improvement of around 2% against the baseline is anticipated
- Conduct SAE J1321 test on the three types of lubricants at the Transportation Research Center Inc. in East Liberty, Ohio, greater than 2% total fuel efficiency is expected

FY 2016 Accomplishments

Engine Oil

- Reformulated two engine oil candidates with the latest Proposed Category 11 (FA-4) packages and found better tribological performance in the Mini Traction Machine (MTM) test while the High Frequency Reciprocating Rig (HFRR) and four-ball test results are mixed
- At NREL, reran ISL 8.9 L engine FE test on both candidates and improvements were observed

**Gefei Wu (Primary Contact),
Fran Lockwood, Anant Kolekar,
Kwame Duho, Xiurong Cheng,
Amol Savant*, Jonathan Burton****

Valvoline Inc.
3499 Blazer Parkway
Lexington, KY 40509-1850
Phone: (859) 357-3516
email: gwu@valvoline.com

DOE Technology Development Manager:
Michael Weismiller

NETL Project Manager:
Nicholas D'Amico

Subcontractors:

- *Valvoline Engine Laboratory, Ashland, KY
- **National Renewable Energy Laboratory (NREL), Golden, CO

- Candidate 1 – ISL 8.9 L FE testing results: Federal Test Procedure (FTP) cycle FE 1.6%, Supplementaty Emissions Test (SET) cycle FE 1.3%
- Candidate 2 – ISL 8.9 L FE testing results: FTP cycle FE 1.8%, SET cycle FE 1.4%
- Two drums each of Candidate 1 and Candidate 2 and four drums of baseline oil were prepared and shipped out for J1321 test

Axle Oil

One drum each of the two axle oil candidates along with two drums of baseline were prepared and shipped out for J1321 test

Transmission Fluid

Two drums of the transimission fluid candidate and four drums of baseline were made and shipped out for J1321 test

Future Directions

- Finish the ongoing J1321 test

- Run SLT B engine evaluation test on both engine oils to appraise their durability performance
- Conduct FE retention and durability tests on all the three types of oils through field test ■

Introduction

Improving automotive fuel efficiency can help reserve 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 a state-of-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 antiwear agent, antioxidant, viscosity index improver, corrosion inhibitor, and friction modifier. With advanced technology of lubricant additives, low viscosity lubricants have been developed by utilizing special antiwear agents and friction modifiers, novel base oils and viscosity modifiers. The formulaton, modeling, benchtop testing, and dynamometer testing have been finished and milestones have been reached so far.

Approach

Valvoline has the ability to formulate automotive lubricants from individual ingredients and conduct bench top, engine dyno, and field tests. As an

independent automotive lubricant marketer, Valvoline has opportunities working with every lubricant additive supplier and can thus combine the best additives to provide the best performance lubricants. Valvoline has been doing fuel economy improvement studies in heavy-duty oils since 2010 [2–4]. In recent years, Valvoline adopted the design of experiments 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 and 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, and track and fleet testing to reach the target.

Results

The reformulated two engine oil candidates with the latest Proposed Category 11 (FA-4) packages found better tribological performance in the MTM test while the HFRR and four-ball test results are mixed. More details can be reviewed in Table 1 and Figure 1.

The rerun of the Cummins ISL 8.9 L engine FE test was done at Valvoline’s expense. This engine dynamometer test is based on two automated cycles: the FTP transient drive cycle [5] and the 2010 SET ramped modal cycle [6]. A minimum of five hot tests were completed for each engine oil for both the FTP and SET test cycles. The FTP cycles reflect the urban driving conditions while the SET cycles resemble highway situations. The baseline was run before (labelled as Ref Oil 1) and after (labelled as Ref Oil 2) the two candidate oils. The test results are

Table 1. HFRR and Four-Ball Wear Test Results

HFRR: 1.25 GPa (load = 700 g), 20 Hz, 40°C for 10 min, 125°C for 2 h				ASTM D 4172: Four-ball
	Friction @ 40°C	Friction @ 125°C	Wear on Ball (µm)	Wear on Ball (µm)
New Oil 1	0.126	0.145	160	507
Old Oil 1	0.128	0.098	153	512
PB 15W-40 Base	0.13	0.13	161	484
New Oil 2	0.12	0.116	136	431
Old Oil 2	0.122	0.066	131	350

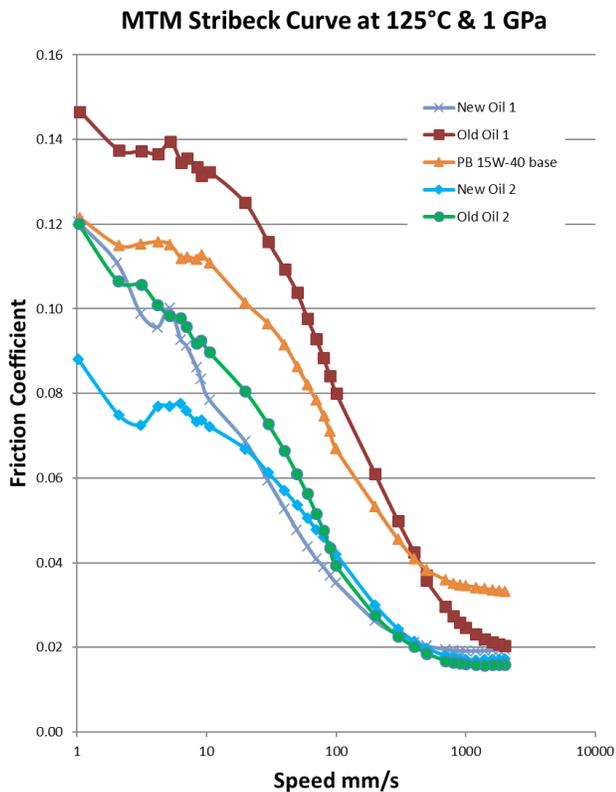


Figure 1. MTM Stribeck curves for engine oil candidates and their baseline

Table 2. Cummins ISL 8.9 L Engine FE Test Results Conducted at NREL

Cummins ISL 8.9 Engine FE Test Result (%)		
	FTP Cycles	SET Cycles
Old Oil 1	1	1.7
New Oil 1	1.6	1.3
Old Oil 2	1.5	1.1
New Oil 2	1.8	1.4

summarized in Table 2 where the latest results are labelled as New Oil 1 and New Oil 2.

The New Oil 1 improved to 1.6% from 1% FE in FTP cycles while New Oil 2 has improvement in both FTP and SET cycles. The 1.8% FE for New Oil 2 in FTP cycles is very close to the 2% target and will boost the chance for vehicle system FE to pass 2% in the next J1321 test. The detailed data for different stages of the SET cycles were summarized in map plots in Figures 2 and 3. In general it is still true that the fuel economy improvement reaches the highest level of close to 4% at low load and

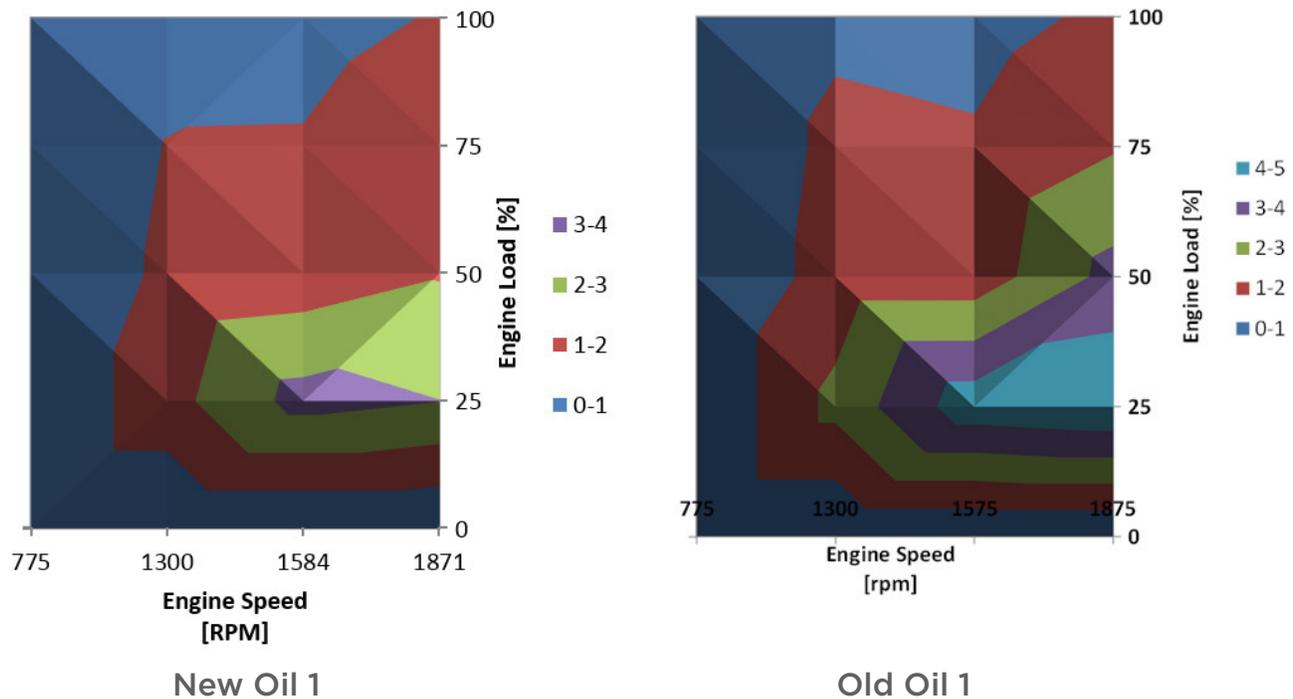


Figure 2. Map of fuel economy improvement from New Oil 1 and Old Oil 1 over the reference oil. Contours are percent improvement in FE.

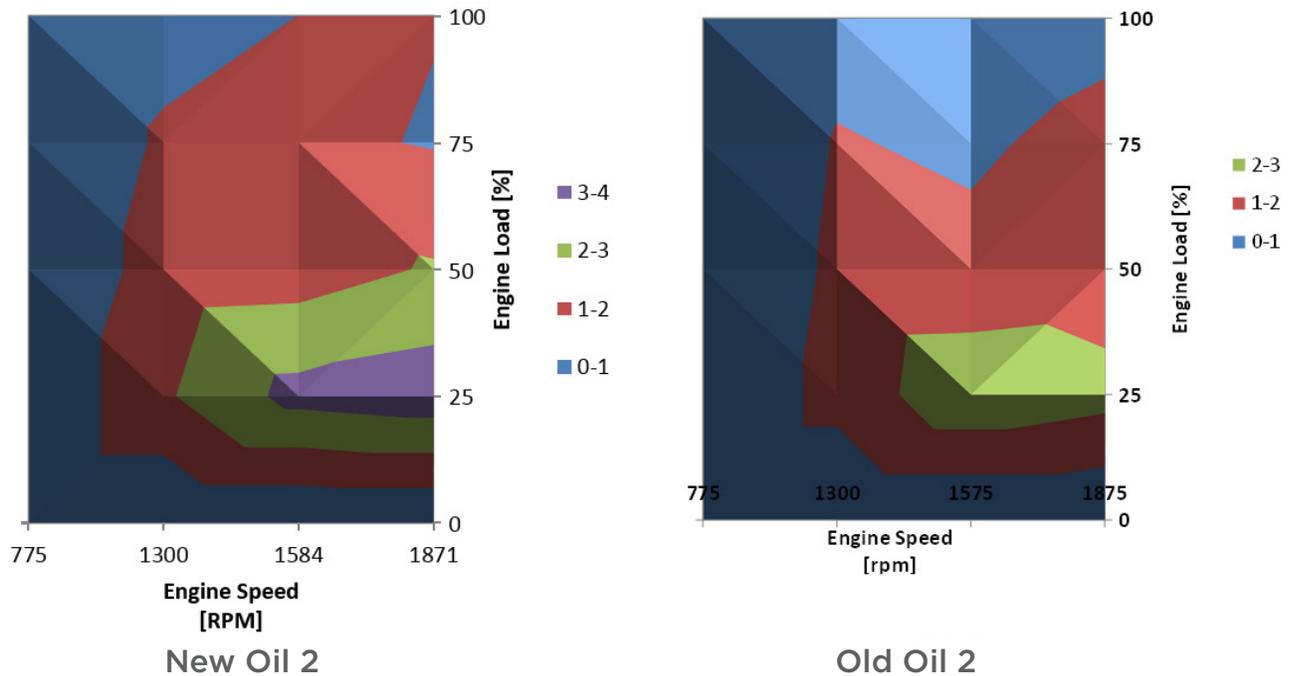


Figure 3. Map of fuel economy improvement from New Oil 2 and Old Oil 2 over the reference oil. Contours are percent improvement in FE.

high speed stages, which corresponds to hydrodynamic lubrication.

When reviewing the detailed data for FTP cycles, it is noted that there might be a carry-over effect since the Ref Oil 2 has lower fuel consumption than the Ref Oil 1. The Ref Oil 1 refers to the baseline run before the two candidates while the Ref Oil 2 stands for the baseline run after testing the candidates. If the FE calculation is based on the Ref Oil 1 only, the New Oil 2 has 2% improvement while New Oil 1 has 1.8% increase. The recalculation results are summarized in Table 3. Since FTP cycles reflect more real-world driving conditions especially for Class 6 trucks, these results are very encouraging.

Table 3. FE Recalculation by Using Ref Oil 1 Only

Cummins ISL 8.9 L Engine FE Test Result (%) for FTP cycles		
	Based on Ref Oil 1 & 2	Based on Ref Oil 1 only
New Oil 1	1.6	1.8
New Oil 2	1.8	2

Conclusions

The reformulated engine oils have better FE performance in the ISL 8.9 L engine FE test. The test results are very close to the 2% target, specifically for the New Oil 2 in FTP cycles. Since FTP cycles reflect more real-world driving conditions especially for Class 6 trucks, these results are very encouraging for the project to pass the overall 2% FE in the SAE J1321 test.

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.
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>.

V.7 Lab-Engine Prediction and Correlation

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) 2016 Objectives

- Understand the factors that affect scuffing and develop scuffing test methodology
- Using the adjustable-angle reciprocating tribometer (AART), evaluate ring coatings to prevent scuffing

FY 2016 Accomplishments

- Acquired a variety of rings coated with different coatings for evaluation
- Developed test methodology to simulate scuffing in the lab, a major failure mechanism of concern to industrial collaborators
- Developed scuffing test methodology and gained understanding of the factors that affect scuffing by performing experiments using the AART
- Broadened network of industrial collaborators

Nicholaos G. Demas (Primary Contact), Robert A. Erck, George R. Fenske

Argonne National Laboratory
9700 South Cass Ave.
Argonne, IL 60439
Phone: (630) 252-6718
Email: ndemas@anl.gov

DOE Technology Development Manager:
Michael Weismiller

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 test results 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 emission strategies. The design of new and improved systems often involves a progression of increasingly complex and costly research and development to demonstrate the technological feasibility and cost effectiveness of a given approach. Developing 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 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

Discussions with both academia and industry personnel have emphasized the importance of understanding scuffing, a catastrophic phenomenon that must be avoided, and determining how different technologies can be implemented to avoid its occurrence. For example, the use of low-viscosity oils that are currently implemented in engines to reduce parasitic friction losses is driving the contact between the piston ring and cylinder liner from the hydrodynamic lubrication regime towards the mixed and boundary regimes that can potentially cause scuffing. Another example is the use of coatings to prevent scuffing. 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.

Over the last year, the AART was used to study scuffing. The development of the AART might serve as a tool to evaluate different technologies such as the types of coatings, materials, and lubricants that can be implemented to prevent scuffing. Additionally, the AART might be able to provide valuable information for down-selecting a particular technology [1,2]. Implementation of a new technology would require ensuring long-term benefits in terms of durability.

Scuffing is a function of load, speed, surface roughness, other topographical parameters, temperature, and the amount of oil present at the contact. The latter depends on the test configuration, for example, how the oil is supplied, i.e., whether the oil is replenished during

the test, whether it forms a pool or is allowed to drain. Therefore, one needs to be concerned with the initial amount of oil present between the contact pairs, the oil supply rate, and the method by which the oil is delivered and distributed over the area of contact.

The amount of oil delivered to the contact as well as the operating temperature is important to simulate engine conditions at the TDC. Argonne's tribology group explored the effect of the oil supply rate to the contact and the temperature necessary to obtain reproducible results, and determined if the oil supply rate and temperature values are consistent with the limited engine data available in the open literature. The initial oil conditions and subsequent precise oil delivery to the tribological contact to replicate the severe starved condition encountered in an engine at TDC are very important to replicate scuffing in the laboratory.

Testing performed during this period sought to understand the mechanism that causes failure by monotonically increasing the load while minimizing the time required per test. 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. While previously the criterion for scuffing using the AART was a coefficient of friction momentarily reaching 0.2, this criterion has been relaxed to 0.15 because in some experiments, where the coefficient of friction reached values above 0.15, unwanted wear was generated.

Experiments performed using amounts of oil between 0.1 $\mu\text{L}/\text{min}$ and 1.0 $\mu\text{L}/\text{min}$ at 190°C showed that the results can greatly vary and indicated that oil delivery to the contact must be well controlled. It was previously shown that the traditional method of placing individual drops, which spread throughout the contact to form a pool of oil (0.1–0.5 mL), provides sufficient lubrication, and scuffing cannot be reached. Additionally, it was shown that even 1 μL of oil provided sufficient lubrication to prevent scuffing under the conditions investigated, which included contact pressures and temperatures relevant to an engine at TDC. The difference between 0.1 $\mu\text{L}/\text{min}$ and 1.0 $\mu\text{L}/\text{min}$ is demonstrated in Figure 1a. This figure shows that 0.1 $\mu\text{L}/\text{min}$ produced an erratic coefficient of friction, indicating that this oil delivery rate is on the edge of starvation, whereas 1.0 $\mu\text{L}/\text{min}$ is ample oil delivery, and the contact is well lubricated, as evidenced by the constant coefficient of friction. These oil supply rates are consistent with numbers provided by other researchers [3,4]. In their research, the oil supply rate was estimated based on oil consumption measurements provided by engine research [5–8]. Figure 1b demonstrates the effect of temperature on scuffing load after an initial amount of

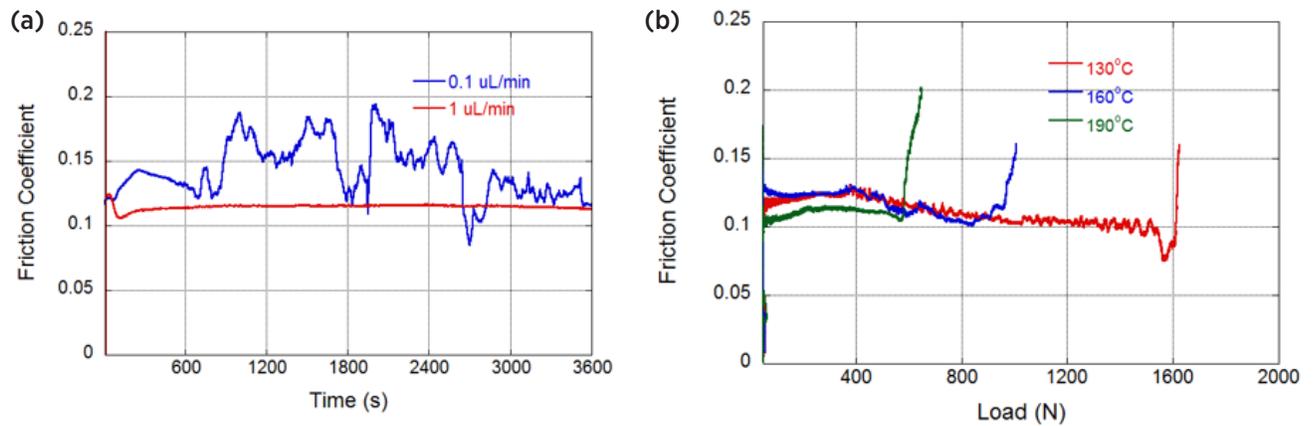


Figure 1. Coefficient of friction as a function of (a) time for oil supply rates of 0.1 $\mu\text{L}/\text{min}$ and 1.0 $\mu\text{L}/\text{min}$ and (b) load for three temperatures (130°C, 160°C, and 190°C)

0.2 μL of oil was introduced to ensure stable behavior at 0.1 $\mu\text{L}/\text{min}$. As temperature increases, the scuffing load decreases, as expected. That can be due to oil thinning, oxidation, and thermal decomposition of the lubricant, which are processes accelerated at higher temperatures.

The AART was also used to evaluate three ring materials. Rings coated with physical vapor deposited (PVD) CrN, ceramic Cr, and diamond-like carbon (DLC) were evaluated by a test protocol that introduced an initial 0.2 μL of oil before setting a constant supply rate of 0.1 $\mu\text{L}/\text{min}$. A scuffing load limit based on several test runs was obtained. The coefficients of friction as a function of load for the CrN, ceramic Cr, and DLC coating are shown in Figures 2a, 2b, and 2c, respectively.

The scuffing load for the CrN was 670 N \pm 85 N. The scuffing load for the ceramic Cr was 600 N \pm 60 N. The coefficient of friction in the case of the DLC exhibited an erratic behavior, and no scuffing limit could be established. Examination of the rings after the test indicated that the DLC ring underwent severe wear. Because wear and scuffing are competing mechanisms, the ring did not scuff because it was not as resistant as the other two materials, but wore off instead. Images of the rubbed area of the ring for the three cases are shown in Figure 3. The formation of a tribofilm is evident on both the CrN and the ceramic Cr rings. The tribofilm was removed with ethylenediaminetetraacetic acid to inspect the area underneath the tribofilm. Figures 3a and 3b indicate that no wear of material occurred and the machining features of the ring remained intact. However, in the case of the DLC, as seen in Figure 3c, the rubbing area appears bright white under the microscope whereas the original had a black appearance. Further profilometric examination revealed that several microns of material

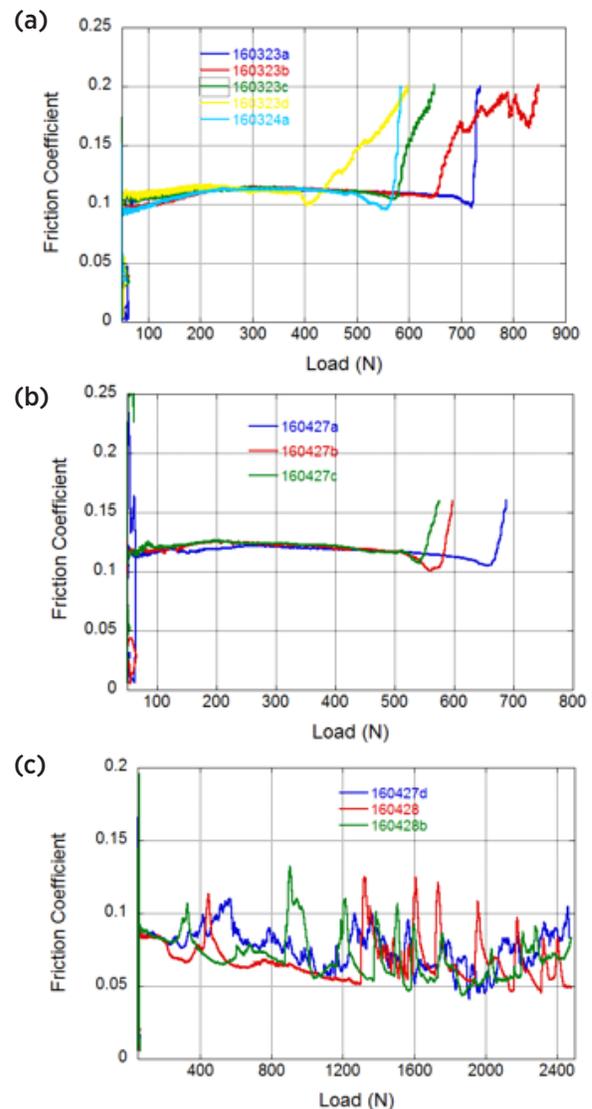
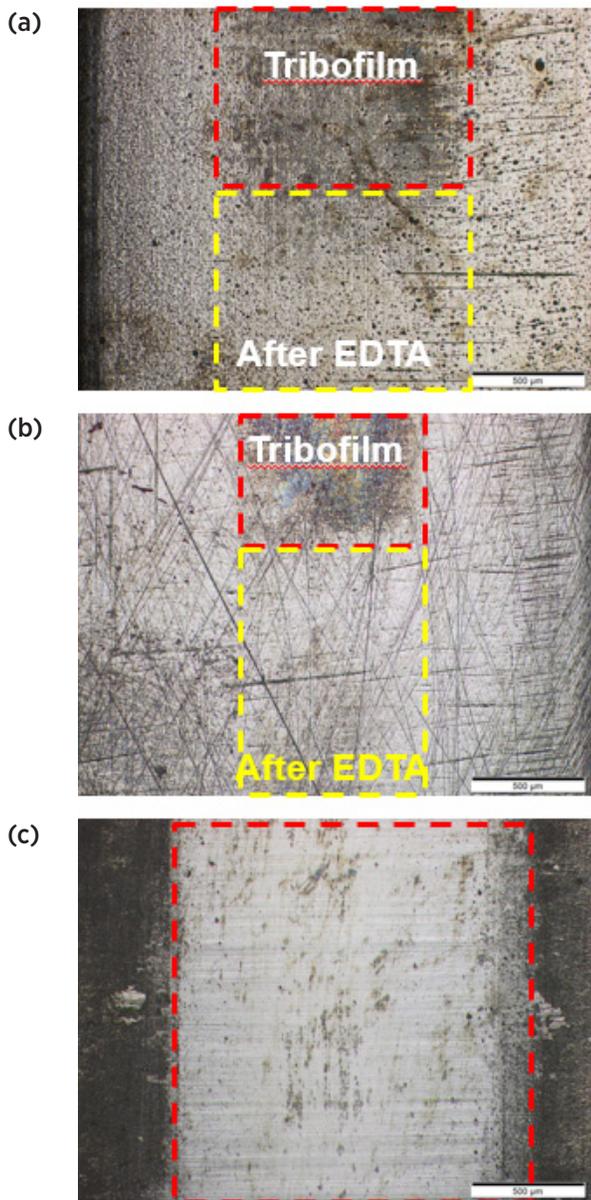


Figure 2. Coefficient of friction as a function of load for the following coatings: (a) PVD CrN, (b) ceramic Cr, and (c) DLC



EDTA – ethylenediaminetetraacetic acid

Figure 3. Micrographs of the ring test tracks after testing for (a) PVD CrN, (b) ceramic Cr, and (c) DLC

were removed, as seen in Figure 4, compared to the PVD CrN rings that showed no wear.

A new modification that was done this year to the reciprocating tribometer was the installation of a motor to allow for automated tilting of the stage, which was previously done manually.

To connect general morphological changes on the liner with the time that they occurred, a camera was employed to record the test. It is believed that the ability to record

images of the surface condition throughout the test can greatly increase our understanding of changes in surface topography, friction, and wear, and the correlation between these changes and scuffing.

Conclusions

- A test methodology to simulate scuffing, a major failure mechanism of concern to industrial collaborators, has been developed.
- Scuffing is a difficult phenomenon to understand, but increasing the coefficient of friction to greater than 0.15 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 in the laboratory and allows for comparison of technologies that can be implemented to avoid scuffing.
- A test methodology to simulate scuffing must be generated for different technologies and compared to engine results and trends; features observed in the lab must also be compared with features resulting from scuffing of real 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 MoS₂ 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., and 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., Füber, H.-J., and 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

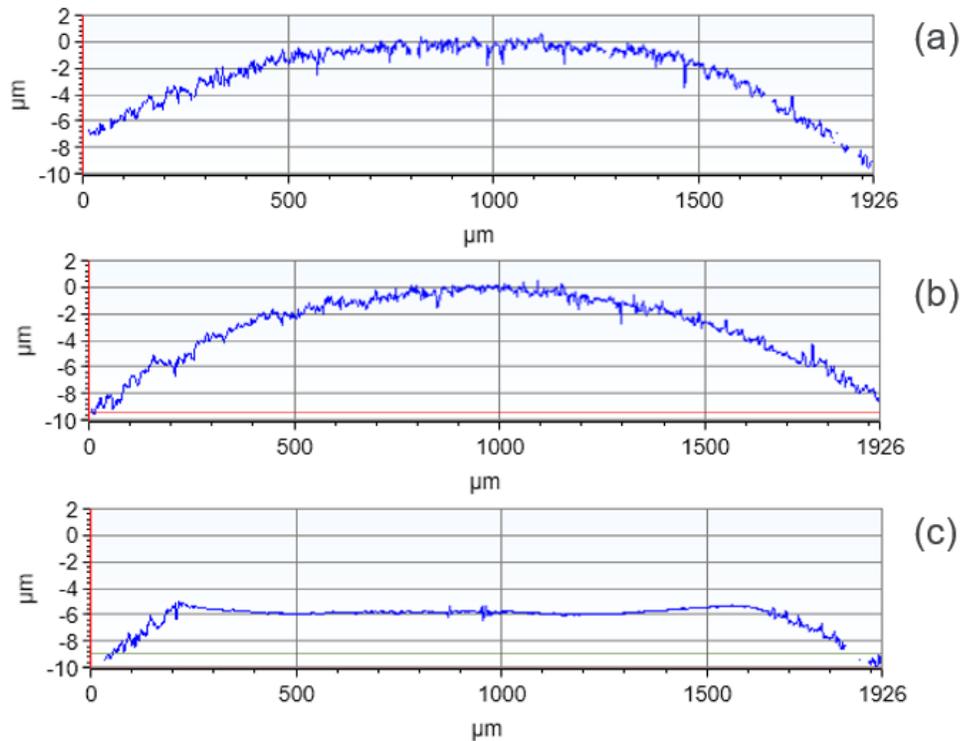


Figure 4. Profilometric line scans for (a) an unrubbed ring, (b) the CrN after testing, and (c) the DLC after testing

consumption of diesel engines, SAE Technical Paper 2005-01-2169, 2005.

6. Herbst, H.M. and Prietsch, 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 2016 Publications/Presentations

1. Demas, N.G., Scuffing methodology development, MIT Consortium Meeting, July 11–14, 2016.

V.8 Engine Friction Reduction Technologies

Overall Objective

The overall objective of this project is to develop advanced coatings, additives, and basefluids that can reduce parasitic friction losses in engines and drivetrains while maintaining or improving the reliability and durability of components.

Fiscal Year (FY) 2016 Objectives

- **Basefluids:** Evaluate the rheological and tribological properties of similarly low viscosity synthetic base fluid (4 cSt polyalphaolefin [PAO4]) and advanced mineral-based oil Group III and III+ (Yubase 4 and 4P). Characterize the rheological properties, friction, and wear of advanced mineral-oil-based basefluid blended with polyol ester fluid mixtures.
- **Additives:** Evaluate the tribological properties of lubricants formulated with colloidal additives. Evaluate the impact of particle shape and morphology on performance and durability of friction reducing colloidal additives. Characterize the nature and structure of tribofilms formed from colloidal additives.
- **Coatings:** Optimize the coating's microstructure, adhesion, hardness, surface roughness, and chemistry. Characterize the chemical and structural nature of carbon-based boundary films and elucidate the 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 2016 Accomplishments

- **Basefluids:** Measured the rheological and traction properties for low viscosity polyalphaolefin (PAO) and two advanced mineral basefluids by kinematic, cold crank viscosity, and high temperature high shear (HTHS) viscosity methods. Also measured the traction behavior for both types of fluids. Evaluated the tribological behavior for the three fluids in unidirectional and reciprocating sliding, as well as in the severe contact conditions of four-ball testing. Determined the rheological properties of advanced mineral-oil-based basefluid blended with polyol ester fluid mixtures.
- **Additives:** Evaluated several encapsulated colloidal additives candidates that reduced both friction and wear compared to many state-of-the-art advanced lubricants.

**George Fenske (Primary Contact),
Oyelayo Ajayi,
Maria De La Cinta Lorenzo Martin,
Ali Erdemir, Osman Eryilmaz,
Nicholaos Demas, Robert Erck, and
Giovanni Ramirez**

Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
Phone: (630) 252-5190
Email: gfenske@anl.gov

DOE Technology Development Manager:
Michael Weismiller

The impact of the encapsulator requires further studies. Studied the impact of shape, size, and morphology of specific friction modifier colloidal additives, including evaluating MoS₂. The results indicated that defected fullerenes morphologies provided quicker friction reduction, although after a long enough period of time, a similar friction behavior was obtained. The nanostructure of tribofilm formed from an antiwear (AW) colloidal additive was evaluated with cross-sectional transmission electron microscopy (TEM). A mostly crystalline well-bonded tribolayer was formed resulting in the elimination of wear during sliding contact.

- **Coatings:** Modeled the mechanisms involved in the tribological performance of advanced catalytically active coatings and published the results in the journal *Nature*. Initiated a Strategic Partnership Program with Evonik Industries, related to the application of nanocomposite coatings to industrial components.

Future Directions

The lubricant technology activities are transitioning to a new multilab lubrication project selected for award by the U.S. Department of Energy (DOE). The project is entitled *Lubricant Technology — Innovation, Discovery, Design, and Engineering*. The new project will have subtasks related to:

- **Basefluids:** Evaluate the impact of additives on the performance of advanced mineral basefluid and

polyol ester blends. Explore other binary and ternary blending involving PAO, mineral base oils, and ester fluids. Develop a thermodynamic model to predict the rheological properties of binary and ternary fluid mixtures, including fuel dilution.

- **Additives:** Evaluate the effect of an encapsulator on the tribological performance and behavior of different colloidal additive systems. Measure nano-mechanical properties and behavior of tribofilm formed from different classes of colloidal additives systems. Evaluate the scuffing performance of potential colloidal additive systems with standard test protocols. Evaluate the thermal properties and behaviors of colloidal lubricant systems.
- **Coatings:** Complete the remaining bench tribological studies and develop friction and wear maps illustrating operational ranges of optimized coatings. Confirm the durability and effectiveness under conditions that are typical of actual engine components. Complete the surface and structural characterization of carbon-based boundary films and elucidate their lubrication mechanisms. Confirm their 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 with 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 the reliability and durability of their 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 that mitigates boundary friction and, 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

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, and hence there is a need for excessive use of additives [1]. Another problem is the increased evaporation rate. The development of a synthetic, low-viscosity hybrid base stock with optimized rheological properties can achieve friction reduction in the hydrodynamic regime without compromising performance in the boundary regime. This will enable fuel economy improvements and ensure the reliability of engine components.

This task develops composite base stocks consisting of low viscosity PAO and ester-based synthetic fluids to minimize viscous shear losses. The rheological, traction, and various tribological (friction, wear, and scuffing) properties of the composites fluids will be determined. The same attributes were evaluated for the composite base fluids in the presence of conventional AW and friction modifier additives to lubricants.

Measurements were conducted to compare rheological properties in terms of kinematic, cold crank and HTHS viscosity of benchmark advanced mineral oil Group III, Group III+, and PAO. Figures 1A and 1B show that the kinematic and HTHS viscosity of PAO and the two mineral-oil-based fluids are similar. Figure 1C shows that PAO has slightly lower cold crank viscosity at a very low temperature. As expected, kinematic and HTHS viscosity behavior for the three fluids are similar to one another. However, differences were observed in the cold crank viscosity measurement. At -20°C viscosity was similar, but with decreasing temperatures, differences were more pronounced with PAO having the lowest viscosity (Figure 1C). Figure 2 shows the traction behavior for

the fluids. The results indicate higher values for mineral basefluid Group III, and similar results for PAO and mineral Group III+.

Figure 3 shows the friction and wear (flat and ball) under reciprocating sliding using ball-on-flat contact configuration at a load of 15.6 N, 1 Hz., with a stroke length of 10 mm at 100°C. Under these test conditions, the frictional behavior of the three fluids with and without additives were very similar to one another. In terms of wear, mineral Group III+ basefluid reduced wear substantially compared to mineral Group III and PAO in the flat specimen, although it produced more wear on the ball. With additives, the wear performance for all the fluids in both flat and ball specimens was significantly reduced and it was similar for all the fluids. Similar trends and behaviors for friction and wear were observed in unidirectional sliding. Under a more severe contact condition of four-ball testing, the two mineral-oil-based fluids showed less wear than the PAO. This may be attributed to higher chemical interaction with surfaces in mineral oils compared to PAO (Figure 4).

The tests determined the rheological properties in terms of kinematic, cold crank, and HTHS viscosity of advanced mineral oil Groups III and III+ and polyol ester blends. Figure 5A shows the measured kinematic viscosity as a function of ester and/or mineral oil ratio in the blend. Clearly, there is a mixture composition with minimum viscosity. This result will be important in the development of a thermodynamic model for fluid mixture viscosity predictions. Figure 5B shows the cold crank viscosity measurement of the different mixtures conducted at a temperature range between -40°C and -20°C. At -40°C the mixtures with a higher concentration of ester became too viscous, reaching the limit where they could be measured. Figure 5C shows the HTHS viscosity measurement for the two different mineral base oils blended with ester. Clearly, the HTHS viscosity increased with the ester content in the mixture. This may have some implication for the fuel

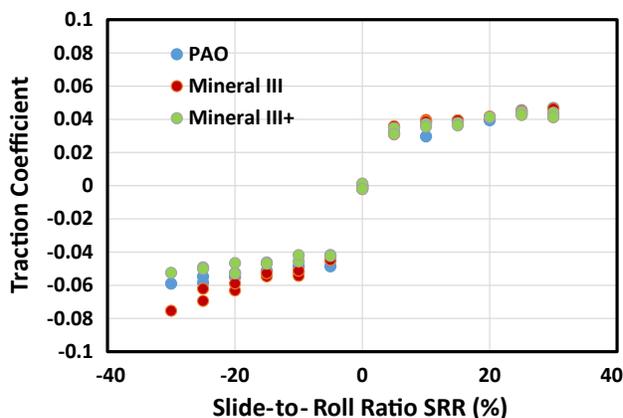


Figure 2. Comparison of traction coefficient for PAO and advanced mineral Group III and III+

economy gains in this mixture since the HTHS viscosity has been correlated with fuel economy gains in engines.

Advanced Additives

Substantial fuel savings and reduced use of petroleum oil can be achieved in the near-term if the fleet of current legacy vehicles can be made more efficient without expensive retrofits. An approach most likely to succeed in both new and legacy vehicles is the development of a lubricant that can reduce engine friction compared to the currently available ones. Also, the use of higher levels (greater than the current 10%) of ethanol bio-based fuel in the current legacy gasoline engines will require a lubricant that can protect the engine components from expected accelerated wear. Another approach being considered for increasing fuel economy in vehicles is the use of lower viscosity engine oils, which will make components susceptible to accelerated wear and damage, even scuffing. Thus, additives are needed that can provide sustainable friction reduction without compromising reliability and durability under various stringent conditions that are expected in new engines. The current project seeks to develop lubricant additives that can

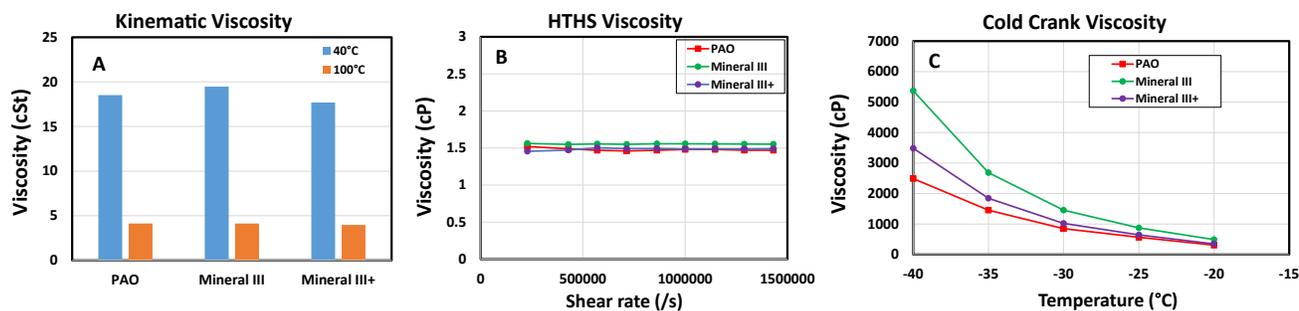


Figure 1. Measurement of basefluids viscosity: kinematic, HTHS, and cold crank

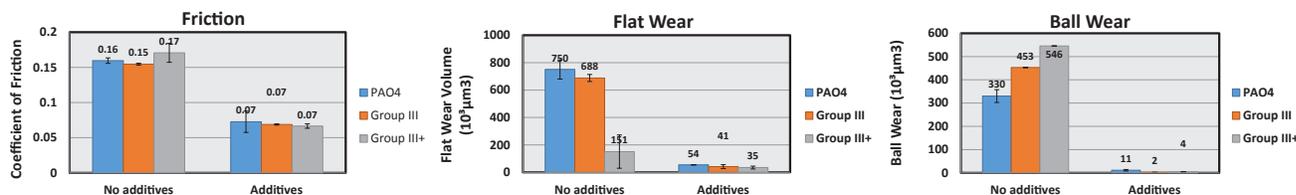


Figure 3. Friction and wear performance for advanced mineral oils Group III and III+ compared to PAO4 under reciprocating sliding

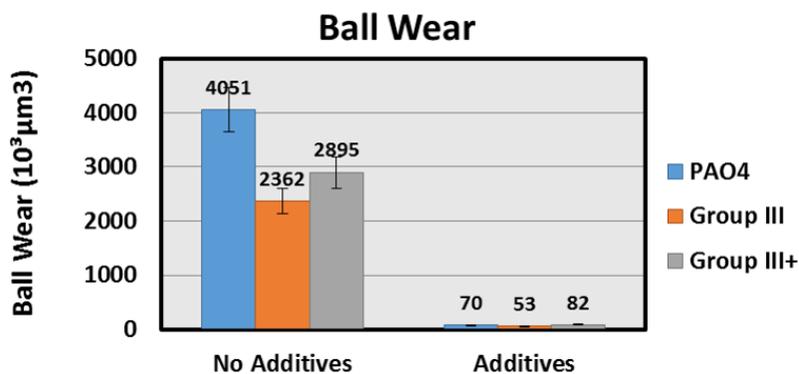


Figure 4. Wear performance for advanced mineral oils Group III and III+ compared to PAO4 under severe four-ball testing

achieve friction reduction without compromising engine reliability and durability.

The main goal of this effort 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 with the attributes 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 performance attributes. Compared to 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. Wear-reducing and scuff-preventing particulate systems 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. It should be noted that some of the current additive systems are based on the nano-particulate platform as proposed here, e.g., detergents in diesel engine formulation.

Friction and wear behavior of several colloidal additive systems were evaluated under different contact conditions, in unidirectional and under more severe contact conditions of four-ball testing. Figure 6 shows the average friction behavior during unidirectional sliding for several candidates with and without an encapsulator at 100°C. Without encapsulation, all the candidate particles for colloidal systems produced higher friction compared to current state-of-the-art advanced lubricants. When encapsulated with oleic acid, friction reduction to the same range as current lubricants was observed for all the candidates. In terms of wear, some additives produced negative wear (material build up), while other additives produced much more wear than the baseline lubricant particularly in the absence of encapsulation. Similar trend and wear behavior was observed under the more severe contact condition of four-ball testing.

The effects of particle morphology on the friction and wear of MoS₂-based colloidal additive systems were evaluated using two different types of particles: (a) hollow inorganic-fullerene-like particle, and (b) solid, with a

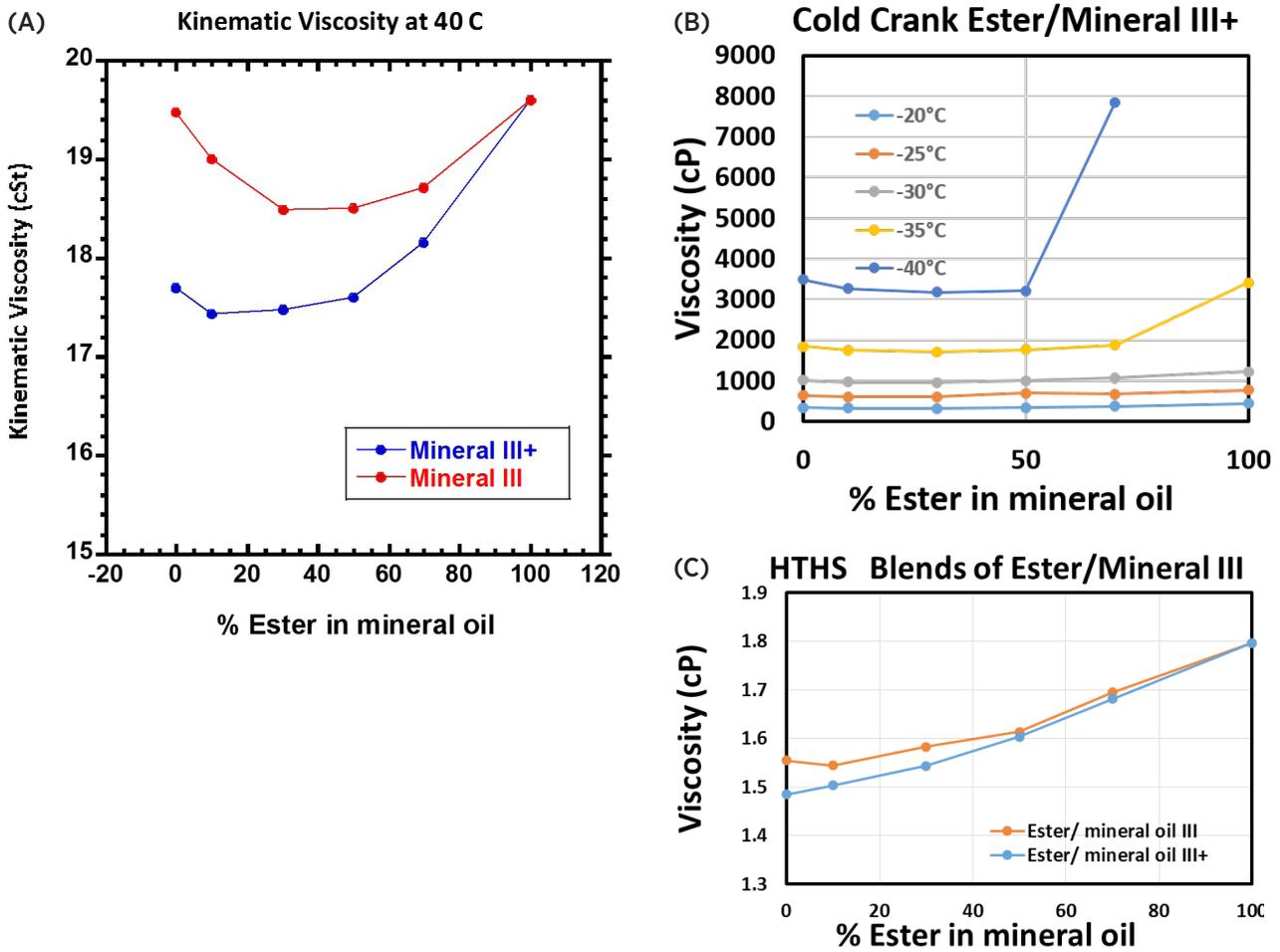


Figure 5. Measurement of blended fluids viscosity: (A) kinematic, (B) cold crank, and (C) HTHS

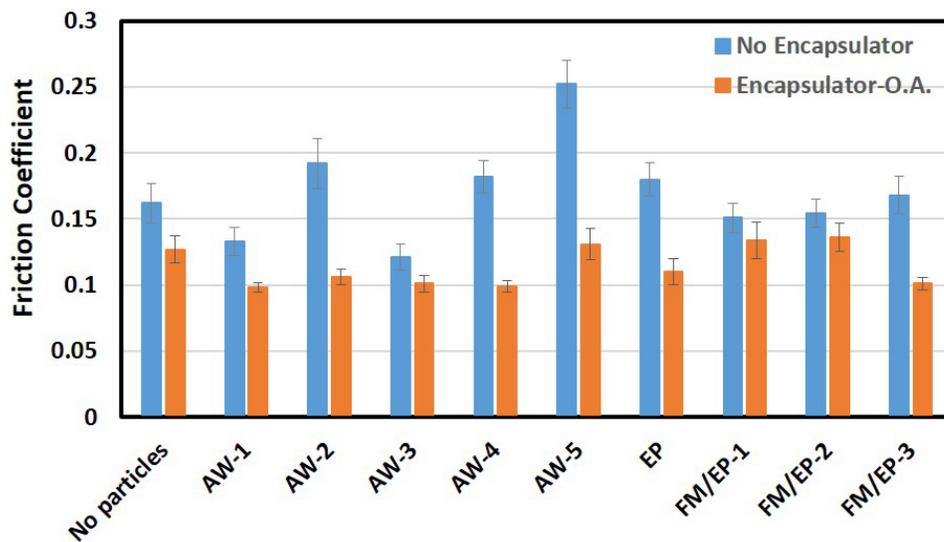


Figure 6. Average boundary friction for colloidal lubricants systems under unidirectional sliding

ball-on-flat contact configuration under reciprocating sliding conditions particle. Both colloidal additives eventually reduced the boundary friction to about 0.05 from the initial value of 0.15 (Figure 7). The transition occurred more quickly in the inorganic fullerene particle compared to the solid one. This is attributed to the easy exfoliation of the MoS₂ layer leading to the formation of a protective low shear tribofilm which also impacted wear protection.

All colloidal additives were observed to form a tribolayer during sliding contact on the steel substrate. Previous studies have shown that the structure of such films determines their tribological performance attributes

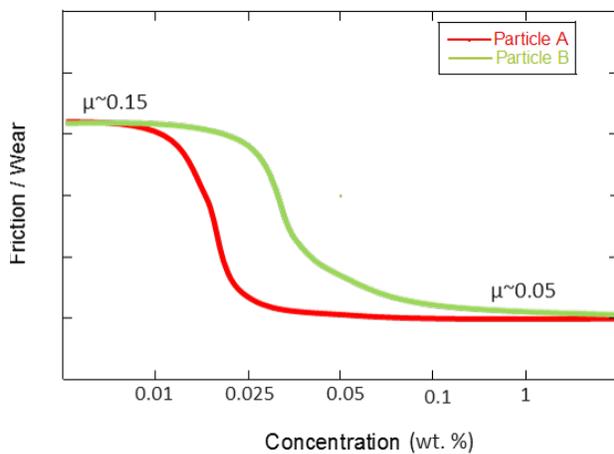


Figure 7. Comparative friction and wear behavior for two inorganic fullerene MoS₂ colloidal systems

[1]. Consequently, the nanostructures of a tribofilm formed from an oxide-based colloidal AW additive were analyzed by the combination of electron microscopy (scanning electron microscopy and TEM). Figure 8a shows the scanning electron micrograph of the surface of the tribofilm. Although there is clear evidence of the formation of tribofilm, the morphology is patchy as indicated in Figure 3A. Cross-sectional TEM (prepared by focused ion beam) of the film is shown in Figure 8b. Detailed examinations show the film consists primarily of a nanocrystalline surface layer of 5–10 nm range.

Under unidirectional sliding and four-ball wear testing, several encapsulated colloidal additives candidates produced friction behavior comparable to many of the state-of-the-art advanced lubricants. Without encapsulation however, higher friction was observed. This suggests the need for further studies of the role of an encapsulator in the tribological performance of colloidal additives systems. The impact of the shape, size, and morphology of the specific friction modifier colloidal additives (MoS₂) was evaluated. The results indicated that fullerenes morphologies with defects provided a quicker friction reduction, although after a long enough period of time, similar friction behavior was obtained. This is attributed to the ease of exfoliation and the formation of a tribolayer in defected fullerene MoS₂ particles. The nanostructure of tribofilm formed from an AW colloidal additive was evaluated with cross-sectional transmission electron microscopy. A mostly crystalline well-bonded tribolayer was formed resulting in the elimination of wear during sliding contact. This result is consistent with the previous observation of wear-resistant tribofilms.

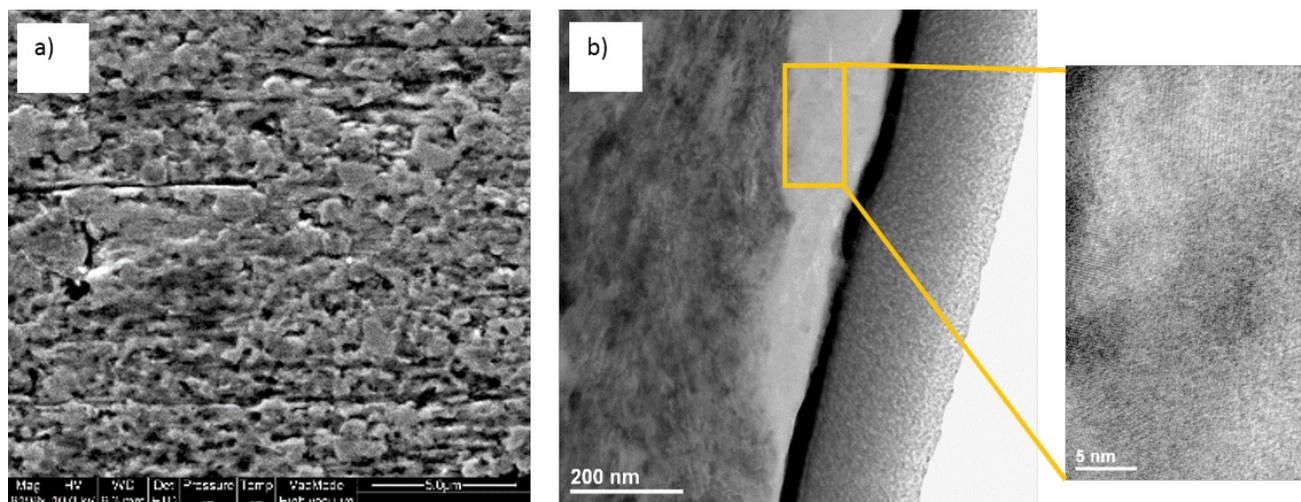


Figure 8. Nanostructure of a tribofilm produced with oxide-based antiwear colloidal additive. Figure 8a shows the scanning electron micrograph of the surface of the tribofilm. Figure 8b shows that the film consists primarily of a nanocrystalline surface layer of a 5–10 nm range.

Optimization of Non-ferrous Coatings

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

Figure 9 compares the typical scuffing load that the 52100 steel and VN-Ni nanocomposite coating can handle when tested using block-on-ring in the presence of PAO 10 cSt base oil. These results confirm that the catalytically active nanocomposite coating not only improves the wear and friction behavior, but it increases the load (pressure) that the system can survive before scuffing occurs.

Figure 10 shows time-of-flight secondary ion mass spectrometry studies that confirmed the presence of carbon-based tribofilms on the wear track of a MoNx-Cu coated ball after it was tested in PAO10. The figure shows the spectrum of inside and outside the contact

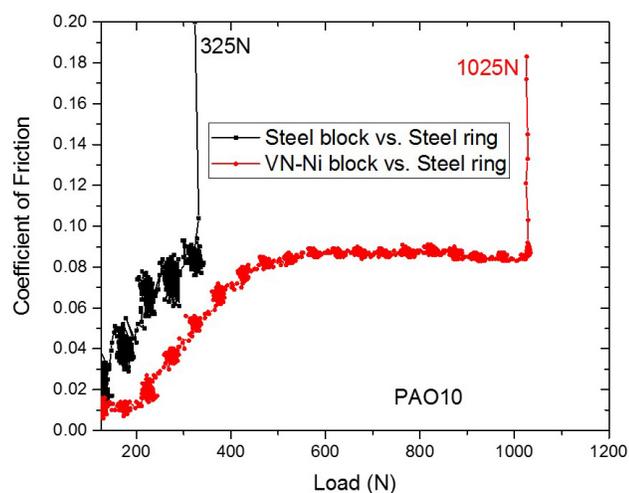


Figure 9. Friction to load behaviors of VN-Ni coated block/52100 ring and 52100 block/52100 ring surfaces under extreme pressure using a block-on-ring test system

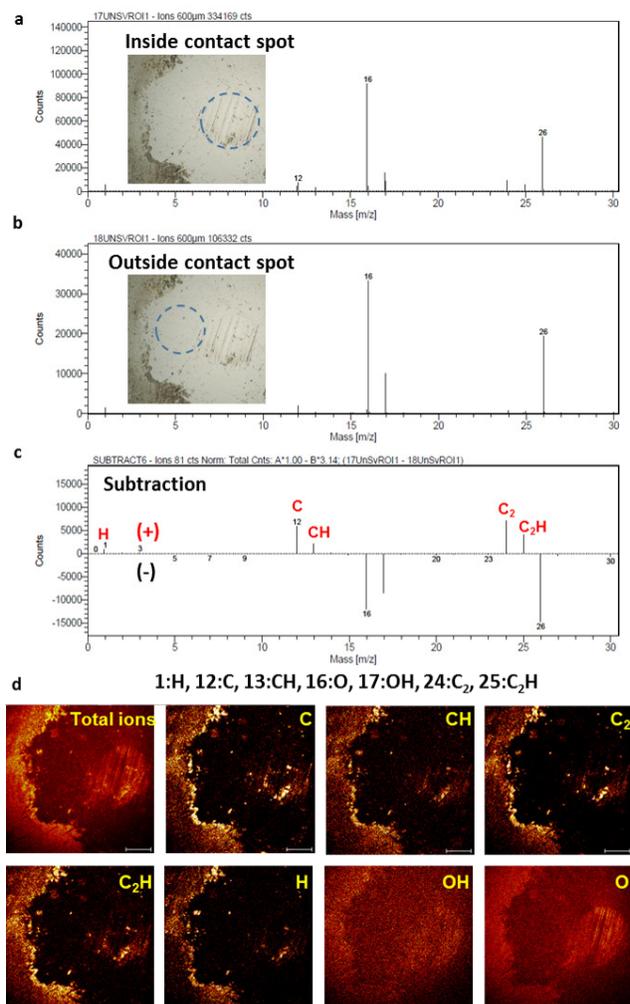


Figure 10. Time-of-flight secondary ion mass spectrometry mapping inside and outside the contact spot (wear mark) on the coated ball

spot, and the spectrum after subtraction verifying the presence of carbon and other hydrocarbon fractions on the contact spot. This result confirmed again the presence of carbonaceous film produced during the rubbing of the catalytically active surfaces in the presence of PAO.

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 2016 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 Energy Efficiency & Renewable Energy, Vehicle Technologies Office, Fuels & Lubricant Program, (2015).
2. C. Lorenzo-Martin, O.O. Ajayi, A. Erdemir, and G.R. Fenske, "Scuffing Performance of Mixed Synthetic Base Fluids." Society of Tribologists and Lubrication Engineers Annual Meeting, May 15–19, 2016, Las Vegas, NV, USA.
3. O.O. Ajayi, C. Lorenzo-Martin, R.A. Erck, and G.R. Fenske. "Effect of Fuel Dilution on Tribological Performance of Engine Oil – Part I and II – Surrogate Fluids." SAE 2016 World Congress and Exhibition. April 12–14, 2016; Detroit, MI, USA.
4. O.O. Ajayi, C. Lorenzo-Martin, D. Singh, and G.R. Fenske, "Advanced Lubrication Additives for Improved Fuel Efficiency," FY 2015 Annual Progress Report, DOE Office of Energy Efficiency & Renewable Energy, Vehicle Technologies Office, Fuels & Lubricant Program, (2015).
5. C. Lorenzo-Martin, D. Dandurand, B. Good, O. Ajayi, J. Bansal, F. Dassenoy, and P. Afanasiev. "Effect of Concentration on Tribological Performance of IF-MoS₂ Nanoparticles Additives." Tribology Frontiers Conference, October 25–27, 2015, Denver, CO, USA.
6. C. Lorenzo-Martin, D. Dandurand, O. Ajayi, J. Bansal, F. Dassenoy, and P. Afanasiev. "Effect of Particle Morphology and Structure on Durability of MoS₂ Nanoparticle Tribofilm." Society of Tribologists and Lubrication Engineers Annual Meeting, May 15–19, 2016, Las Vegas, NV, USA.
7. Ali Erdemir, Giovanni Ramirez, Osman L. Eryilmaz, Yifeng Liao, Badri Narayanan, and Subramanian Sankaranarayanan. *Carbon-based Tribofilms from Lubricating Oils*. **Nature** **536** (2016) 67–71.
8. Ala Alazizi, Andrew Draskovics, Giovanni Ramirez, Ali Erdemir, and Seong H. Kim. Tribochemistry of carbon films in oxygen and humid environments: Oxidative wear and galvanic corrosion. **Langmuir** **32** (8) (2016) 1996–2004.
9. Harpal Singh, Giovanni Ramirez, Osman Eryilmaz, Aaron Greco, Gary Doll, and Ali Erdemir. "Novel Fatigue Resistant Carbon Coatings for Gear and Bearing Applications." **Tribology International** **98** (2016) 172–178.
10. G. Ramirez, O. Eryilmaz, and A. Erdemir, "Extraordinary Wear Performance of Nanocomposite Coatings in Fully Formulated Oils," 71st Society of Tribologists and Lubrication Engineers STLE Annual Meeting & Exhibition, Las Vegas, NV, May 15–19, 2016.
11. G. Ramirez, O. Eryilmaz, and A. Erdemir, "Designer Nanocomposite Coatings for Exceptional Wear Performance in Methane Environment," 43rd International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 25–29, 2016.
12. A. Erdemir, O. Eryilmaz, and G. Ramirez, "Design and Synthesis of Catalytically Active Nanocomposite Coatings: Towards a New Paradigm Shift in Tribological Applications," 43rd International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 25–29, 2016.

V.9 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 durability limits and interaction of tribochemical films with basestock oil
- Determine and develop model for failure mechanisms of lubricated systems in engines
- Validate performance in both bench-top testing and engine environments

Fiscal Year (FY) 2016 Objectives

- Verify the peculiar friction behavior for low viscosity base fluid for other additive systems
- Characterize the basic mechanisms of scuffing for in-use engine components in comparison with bench-top scuffing test samples
- Determine the nano-mechanical properties of tribochemical surface films in engine components using nano-indentation techniques

FY 2016 Accomplishments

- Observed some deviation in friction for low viscosity fully formulated engine oil
- Based on optical and scanning electron microscopy (SEM), established similarities in scuffing damage from in-use engine components and bench-top test specimen
- In nano-mechanical measurements, determined that tribofilm hardness was 5–7 GPa and varied with thickness; elastic modulus followed a similar trend

Future Directions

- Evaluate tribological performance in terms of scuffing and wear under severe contact conditions for additives that produce low friction tribochemical films

Oyelayo Ajayi (Primary Contact), Cinta Lorenzo-Martin, George Fenske

Argonne National Laboratory
9700 S. Cass Avenue
Lemont, IL 60439
Phone: (630) 252-9021
Email: ajayi@anl.gov

DOE Technology Development Manager:
Michael Weismiller

- Continue characterization of the basic mechanisms of scuffing of in-use engine components
- In collaboration with academia and industry partners, develop predictive model for wear and scuffing in engine liners
- Determine and formulate constitutive equations to enable friction prediction and modeling at the lubricated interface
- Develop empirical relationship between base fluid viscosity and boundary regime frictional behaviors ■

Introduction

Most critical components in the sub-systems of engines and transportation vehicles 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 finishes, and lubricant oil formulations—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 [1]. These additives react with the surface material during oil-lubricated sliding and/or rolling contact to form tribochemical surface films. Design and engineering of these tribochemical surface films are the key to friction reduction while maintaining reliability and durability. The main goal of the current project is the development of a 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 study of the basic mechanisms of failure, especially scuffing in engine components and the development of a predictive model for such failures.

Approach

To take technological advantage of the low friction tribochemical surface layer, better understanding of the nature, the composition, and the mechanism of the formation and durability of the film is required. The initial goal of this proposed effort is to develop this understanding. The overall goal is to advance the 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 producing low friction films, characterization of their tribological properties, and performance optimization for a variety of pertinent components. Detailed modeling and validation studies (bench-top and engine tests) will also be performed.

The approach for this project will involve two key components: (1) the development and optimization of a low friction tribochemical film (tribofilm) and (2) the validation of its performance through engine testing at the Massachusetts Institute of Technology. Based on input from original equipment manufacturers, the study of basic mechanisms and the development of a predictive model for scuffing in the piston ring and liner system of an internal combustion engine is also planned. Briefly, this will involve the following tasks:

- Development of a technique for low friction tribofilm deposition
- Detailed characterization of the composition and structure of the film using various analytical techniques
- Detailed characterization of the nano-mechanical properties of the films

- Tribological performance evaluation of the film by a variety of bench-top friction and wear testing
- Study of mechanisms and development of scuffing model for engine piston ring and cylinder liner

Results

In the last annual report [2], a peculiar frictional behavior as a function of temperature was described for a polyalphaolefin containing two model additives: zinc dialkyldithiophosphate and molybdenum dialkyldithiocarbamate. For very low viscosity fluids (less than 4 cSt at 100°C), a hump was observed in the friction vs. temperature curve between 70°C and 120°C. Similar behavior was also observed in mineral oil and ester-based fluids. Analysis of the results indicated a correlation between friction and the presence or lack thereof of the tribofilm. The highest friction hump coincided with the formation of a crystalline tribofilm. The decrease in friction at higher temperature before failure coincided with the formation of an amorphous/crystalline mixture. It was unclear whether this peculiar behavior was unique to the combination of the additives used or if it was universally true. Consequently, during this reporting period, similar studies were conducted with fully formulated lubricants of viscosity ranging from 4 cSt to 9.5 cSt at 100°C.

Figure 1 shows the variation of friction with temperature (and time) for lubricants with viscosity of 4 cSt, 6.5 cSt, and 9.5 cSt. For the two higher viscosity fluids, the frictional behavior is almost identical to one another. For

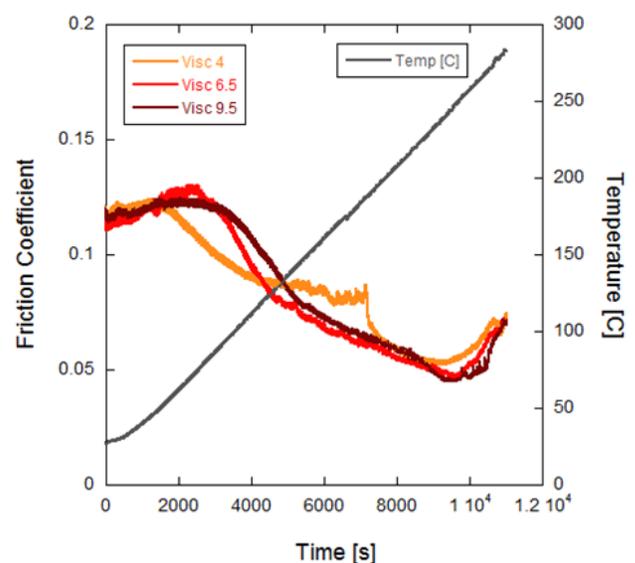


Figure 1. Friction behavior with viscosity for fully formulated engine oil

the lowest viscosity lubricant, slightly different behavior is observed, with some frictional perturbation between 125°C and 175°C. No clear hump in the friction vs. temperature curve is observed. The friction coefficient for the lowest viscosity tested in this group (4 cSt) is still much higher than that of the other viscosities, where the humps were pronounced with the model additives. For these fully formulated lubricants, tests began with a friction of about 0.12 at room temperature, then increased slightly to about 0.14 at 60°C due to a reduction in viscosity with increasing temperature. Beyond this temperature, friction continued to drop almost linearly, to a minimum value of about 0.04 at 250°C. This effect is most likely due to the formation of a low friction tribochemical surface film. A sudden increase in friction occurred beyond this point, which might be indicative of incipient failure as the tribofilm removal rate exceeds the formation rate.

In collaboration with an industrial partner, some effort during this reporting period was also devoted to better understanding the scuffing mechanism in an engine, with the ultimate goal of formulating a predictive model for the failure. To this end, scuffing damage in an in-use engine liner was characterized by optical and SEM. Some bench-top ring and liner tests were also conducted using the same liner and ring material as the ones in the engine. Figure 2a shows an optical micrograph of a scuffed area

on the liner surface from an engine. Similar features were produced in some areas during reciprocating ring-on-liner contact in the bench-top test (Figure 2b). There is a clear similarity of damage modes and mechanisms at least in the optical microscopy images, although the severity of damage in the bench-top specimen appears greater. Some areas on the engine and bench-top specimens were not scuffed but contained prominent tribochemical surface films, as shown in Figure 3. Similarities were also observed between the tribofilm layer produced in the engine and bench-top test.

Further analysis indicated that removal of the tribofilm is a necessary condition for the occurrence of scuffing in a cylinder liner. In view of this critical role of tribochemical films in the observed pathway toward scuffing within in-use engines, efforts were devoted to studying the dynamics of the tribochemical film formation and removal in collaboration with an industrial original equipment manufacturer partner. The industrial partner evaluated the effects of several parameters, including temperature, load, oil flow rate, and duration, on film formation and characteristics. Results showed that the tribofilm is very dynamic, forming very quickly and continuously changing with time. Local removal of tribofilm on a honing plateau was evident with time, as shown in Figure 4. Tribofilm removal rate and subsurface plastic deformation were more pronounced at higher

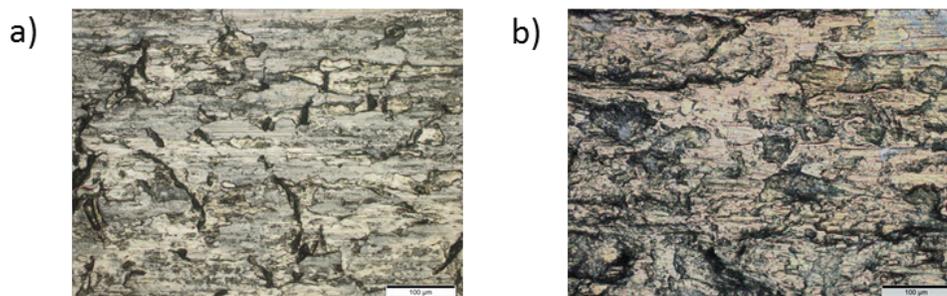


Figure 2. Optical micrographs of scuffed liner components from (a) engine and (b) lab tests

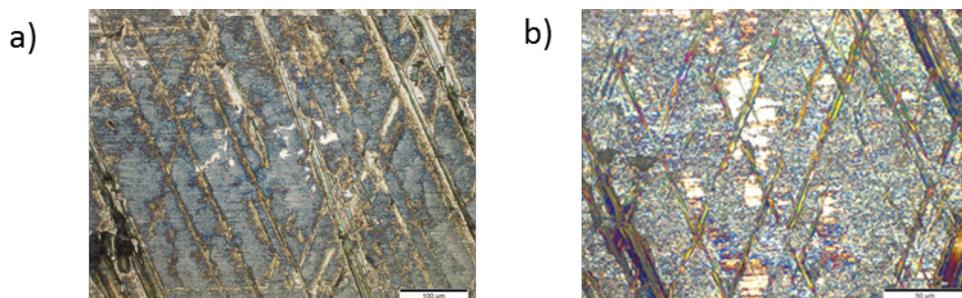


Figure 3. Optical micrographs of tribofilm produced from (a) engine and (b) lab tests

temperatures. Formation of a deposit in the oil groove was also more pronounced at higher temperatures (Figure 4).

SEM analysis of the liner surface showed significant damage but not full scuffing, although a location of scuffing initiation was identified, as indicated in Figure 5. Coupled with the shear strain pattern observed on the liner honing plateau, as noted in last year's report, the scuffing initiation mechanism can form the basis for scuffing prediction and will be incorporated into Massachusetts Institute of Technology's predictive model under development.

To better understand the role of the tribochemical film in the scuffing process in the engine cylinder liner,

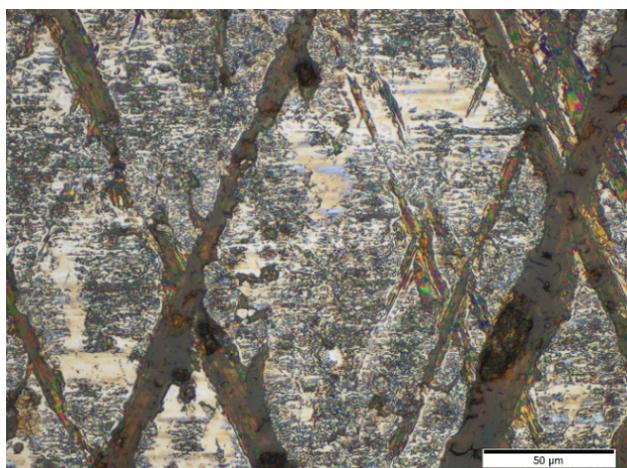


Figure 4. Optical micrograph of tribofilm and localized removal on a honing plateau

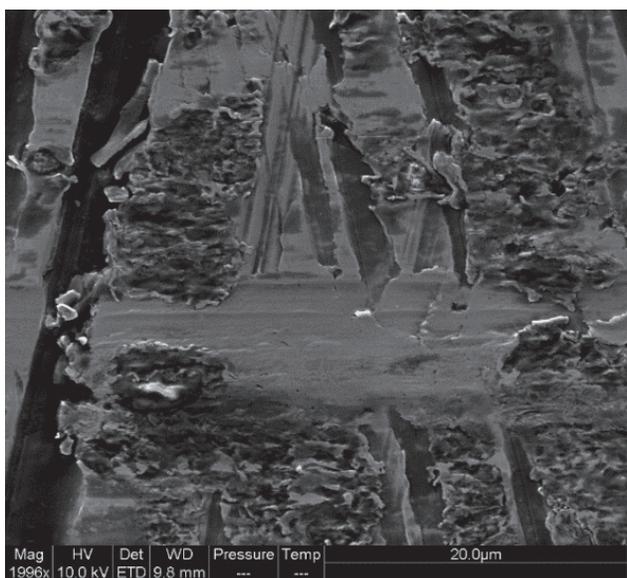


Figure 5. SEM micrograph of apparent scuffing initiation

measurements of the mechanical properties of the film are essential. The properties in terms of hardness and elastic modulus were measured by nano-indentation techniques on tribofilms from in-use engine specimens. Hardness measurements relate to the plasticity of a material, while the elastic modulus reflects the elasticity. With the simultaneous measurement of hardness and elastic modulus, elasticity and plasticity of the tribofilm can be evaluated. A Berkovich indentation tip was used for the measurement by an indentation depth control technique, in which a load displacement curve was generated for indentation depths of 20–150 nm. Figure 6a shows an optical micrograph of a honing plateau with tribochemical film present. The crosshair in the figure is an example of a nano-indentation measurement location. Figure 6b shows several nano-indentation measurements to different depths; hence, there are differences in indentation size. The load displacement curves for measurements to different depths (20–150 nm) are shown in Figure 6b. The hardness and elastic modulus from these measurements at different depths are shown in Figure 6d. Although the average hardness for the tribofilm is about 6.22 GPa, hardness clearly varies with depth. Up to 55 nm, there is a clear trend in hardness, but beyond that point, the results show considerable scatter. This finding might be reflective of the heterogeneity in the structure of the tribofilm or no uniform influence of the substrate material. The elastic modulus results are somewhat similar to hardness but with less pronounced scatter at deeper depth.

Conclusions

Only a subtle effect of viscosity on friction behavior as a function of temperature was observed in one fully formulated engine oil tested, as opposed to the peculiar behavior reported last year with model additives. The frictional behavior of 4-cSt, 6.5-cSt, and 9.5-cSt viscosity engine oils with the same additive package was similar to each other, except for some frictional perturbation in the mid-temperature range for the lowest viscosity oil. Continued analysis of the scuffing process and mechanisms in ring and liner systems in engines suggests a significant role for the tribochemical films. Removal of this film was observed to coincide with scuffing initiation. The mechanical properties of the in-use engine tribofilm were also measured by nano-indentation techniques. The hardness of the particular film was determined to be about 6 GPa and the elastic modulus was about 166 GPa. Both properties were also observed to vary with thickness of the film. Further analysis and characterization of the mechanical properties and behavior of a variety of tribochemical surface films are planned.

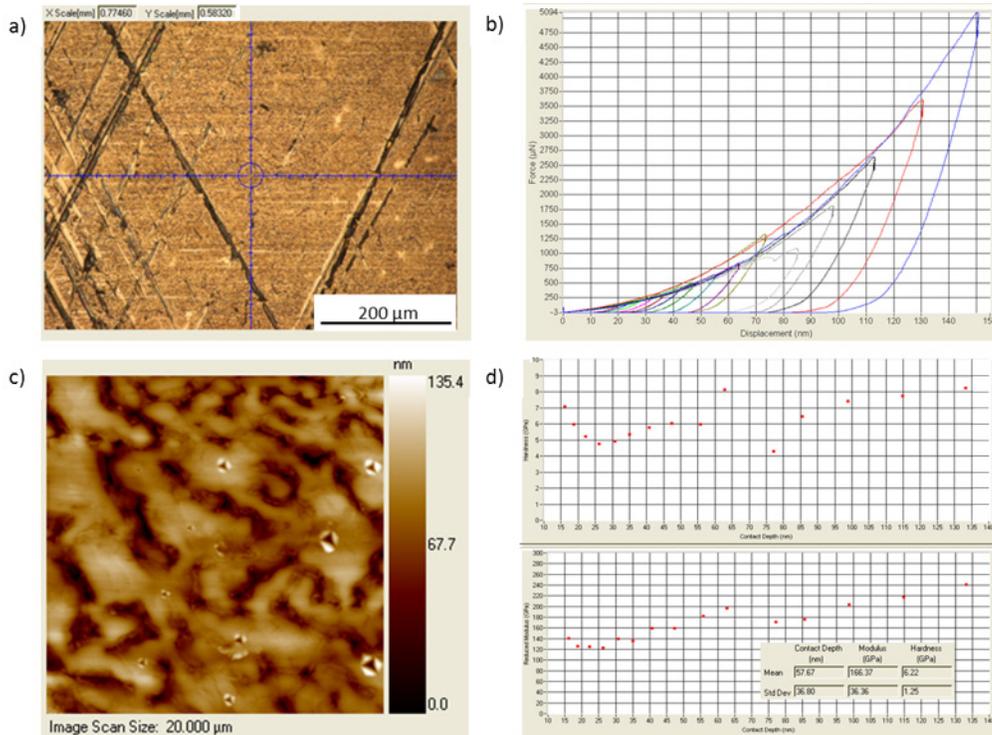


Figure 6. Nano-indentation measurement of tribochemical films on in-use engine liners

References

1. O.O. Ajayi, C. Lorenzo-Martin, and G.R. Fenske, “Advance Lubrication Additives for Improved Fuel Efficiency,” FY 2012 Annual Progress Report, DOE Office of Vehicle Technologies, Fuels and Lubricant Program, II-18-20 (2013).
2. Oyelayo Ajayi, Cinta Lorenzo-Martin, and George Fenske, “Phenomenological Modeling of Lubricant Film Formation and Performance,” Fuel and Lubricant FY 2015 Annual Report (2015).
3. C. Lorenzo-Martin, O.O. Ajayi, A. Erdemir, and G.R. Fenske, “Scuffing performance of mixed synthetic base fluids,” Society of Tribologists and Lubrication Engineers Annual Meeting, May 15–19, 2016, Las Vegas, NV, USA.
4. C. Lorenzo-Martin, D. Dandurand, O. Ajayi, J. Bansal, F. Dassenoy, P. Afanasiev, “Effect of Particle Morphology and Structure on Durability of MoS₂ Nanoparticle Tribofilm,” Society of Tribologists and Lubrication Engineers Annual Meeting, May 15–19, 2016, Las Vegas, NV, USA.
5. Oyelayo Ajayi, Cinta Lorenzo-Martin, and George Fenske, “Phenomenological Modeling of Lubricant Film Formation and Performance,” Fuel and Lubricant FY 2015 Annual Report (2015).

FY 2015 Publications/Presentations

1. O.O. Ajayi, C. Lorenzo-Martin, G. Fenske, J. Corlett, C. Murphy, and S. Przesmitzki, “Bio-derived Fuel Blend Dilution of Marine Engine Oil and Impact on Friction and Wear Behavior,” Journal of Tribology 138(2), 021603-1-11 (April 2016) doi: 10.1115/1.4031781.
2. O.O. Ajayi and C. Lorenzo-Martin, “Scuffing of Diesel Engine Cast Iron Liner: Role of Tribochemical Surface Film,” Society of Tribologists and Lubrication Engineers Annual Meeting, May 15–19, 2016, Las Vegas, NV, USA.

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.

V.10 Characterizing Impact of Engine Lubricant and Fuel Properties on LSPI

Overall Objectives

- Improve the understanding of the impact that engine lubricants and fuel properties have on 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) 2016 Objectives

- Analyze and report on initial LSPI experiments
- Evaluate fuel properties on LSPI such that consistent lubricant-specific results can be achieved
- Demonstrate initial interactions between engine operating conditions, lubricant formulation, and fuel properties on LSPI
- Isolate lubricant properties of interest for LSPI parametric study

FY 2016 Accomplishments

- Demonstrated in-cylinder thermodynamic conditions critical to LSPI event promotion
- Demonstrated that fuel–wall–lubricant interaction is critical for LSPI cluster event
- Demonstrated that trapped residual fraction significantly affects LSPI events
- Disseminated findings to industry and the community through multiple presentations
- Acquired specific lubricant additives and base stock combinations for LSPI testing
- Provided all custom lubricants to the National Renewable Energy Laboratory for ignition delay testing
- Strengthened strategic partnerships with industry to isolate specific lubricant properties of interest to LSPI; designer lubricants formulated and delivered to ORNL for FY 2017 testing

Derek Splitter (Primary Contact), Brian Kaul, Jim Szybist, Gurneesh Jatana

Oak Ridge National Laboratory (ORNL)
2360 Cherahala Boulevard
Knoxville, TN 37932
Phone: (865) 946-1347
Email: splitterda@ornl.gov

DOE Technology Development Manager:
Michael Wiesmiller

Future Directions

- Evaluate parametric lubricant study of lubricant detergent types on LSPI with and without wall wetting
- Down-select lubricant properties of interest for further in-depth campaigns
- Provide unused and used sump lubricant to the National Renewable Energy Laboratory for ignition delay testing; if successful, couple ignition delay results with statistical LSPI results from engine studies ■

Introduction

Currently, the U.S. light-duty market is evolving through downsizing and downspeeding [1], as evidenced by increased continually variable transmission or 6+ speed transmissions, gasoline direct injection, 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 LSPI [7,8]. LSPI results in either a singular or short burst of undesirable or uncontrolled combustion events, exhibiting extreme in-cylinder pressure. The result of extended operation with LSPI can be engine damage or failure, thereby 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 landing 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

This work has utilized a single-cylinder version of a modern turbocharged gasoline direct injected (GDI) engine, which employs in-cylinder pressure-based diagnostics of LSPI event characteristics of fuels and lubricants of interest. The single-cylinder engine is based on a Ford 1.6 L Ecoboost engine, which is a center-mounted GDI engine. Engine experiments 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 position, backpressure, etc.).

Results

This year several experiments were conducted in the Ford 1.6 L single-cylinder engine to explore thermodynamic, fuel preparation, and lubricant 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. This was interesting as the two lubricants were of very different calcium contents (1,200 ppm and 2,500 ppm, respectively), and others have shown that calcium content above 2,000 ppm is a significant factor in LSPI propensity. However, in this initial ORNL research engine little difference in LSPI propensity was observed between these two lubricants. Therefore, prior to multiple lubricant specific investigations, the research focus was to understand the thermodynamic and fuel–lubricant interactions, as demonstrated in FY 2015, that could be responsible for the observed similarity in LSPI frequency with these lubricants.

A thermodynamic campaign was conducted that explored the top dead center (TDC) pressure and temperature

conditions indicative of LSPI. These experiments were conducted with Haltermann EEE Tier II premium grade fuel and Mobil 1™ 5W-20 lubricant. Experiments consisted of intake pressure and backpressure sweeps at constant load and phasing. Operating conditions were fixed at “beyond Research Octane Number,” using an automated low-high-low square wave operating schedule consisting of 5 min at low load followed by 20 min at high load. All data were collected through two consecutive high load segments at 2,000 rpm with constant 50% mass fraction burned phasing of 38° crank angle after TDC firing at 21 bar gross indicated mean effective pressure. Intake temperature was swept from 35°C to 80°C in 15°C increments, with spark timing adjusted at each intake temperature to maintain constant 50% mass fraction burned and load at each intake temperature. Also, throughout the sweep, trapped residual fraction was kept constant by maintaining the same pressure differential across the engine at all intake temperatures. The pressure–temperature trajectory of the sweep is highlighted in Figure 1, with corresponding LSPI event counts presented in Table 1. Results showed that LSPI event count correlated with intake temperature and pre-spark heat release rate (PSHR), as highlighted in Szybist and Splitter [9]. However, with relatively low backpressure, there were relatively low LSPI events number counts. Follow on experiments were then conducted at constant intake temperature while increasing backpressure (i.e., numerically decreasing ΔP_{engine} in the present terminology). As shown by Figure 2 and in

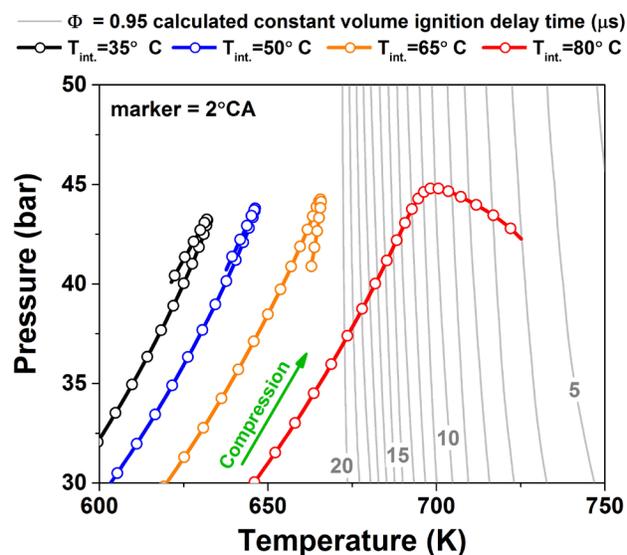


Figure 1. In-cylinder pressure–temperature trajectory for various intake temperatures, data plotted up to spark discharge, and 2° crank angle (CA) resolution noted by data markers

— $\Phi = 0.95$ calculated constant volume ignition delay time (μs)
 $T_{\text{int}} = 35^\circ\text{C}$, sweep ΔP — — $\Delta P = 23 \text{ kPa}$ — — $\Delta P = 11 \text{ kPa}$ — — $\Delta P = 9 \text{ kPa}$
 $\Delta P = 24 \text{ kPa}$, sweep T_{int} — — 35°C — — 65°C — — 80°C

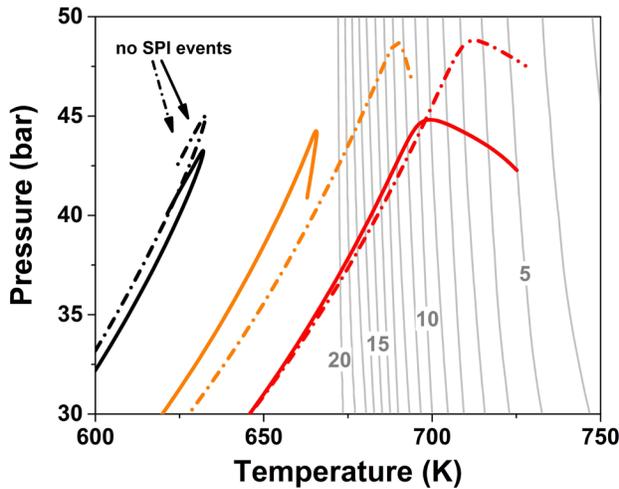


Figure 2. In-cylinder pressure–temperature trajectories for intake temperature (solid) and backpressure (dashed) methods to increase TDC fuel reactivity state

Table 1, for a given TDC condition, the backpressure approach significantly increased the LSPI event count, so much so that the highest backpressure could not be operated for the entire load sweep due to pressure transducer failure after ~5 min. The results highlight that backpressure increased the TDC temperature and pressure due to increased trapped residual increasing the ratio of specific heats (γ) of the working fluid. Furthermore, the stability of the backpressure approach was also found to be significantly reduced an effect of increased cycle-to-cycle coupling of the trapped residual composition and temperature. The combined intake temperature and backpressure results highlighted that the thermodynamic conditions are critical to LSPI propensity, however no “cluster” LSPI events, a commonly documented phenomena [7,8] where LSPI events occur in an on-off-on-off series for multiple cycles, were found. This interaction is thought to be a result of lubricant and fuel interaction in the top ring zone as measured by Splitter et al. [10].

The lack of “cluster” LSPI events was hypothesized to be a result of a lack of fuel impingement on the cylinder liner with the center-mount GDI configuration of the test engine. Experiments to explore fuel–wall interaction were conducted by reorienting the GDI injector to spray towards the cylinder wall, as illustrated in Figure 3. In the modified GDI orientation, the intake temperature sweep at constant backpressure was replicated. The temperature–pressure trajectories of the modified orientation are compared to the original equipment manufacturer

Table 1. SPI Tendency of Intake and Backpressure Sweep, Data Color Coded to Coincide with Figure 2, Grey Background is Dashed Data in Figure 2

θ injector ($^\circ$ from stock)	0	180	0	180	0	180	0	180
T_{intake} ($^\circ\text{C}$)	35	35	50	50	65	65	80	80
PSHR (% of total HR)	0	0	0	0.7	0.2	1.6	1.4	2.1
SPI count (#/30000 cycles)	0	0	0	4	3	3	4	4
SPI cluster (Y/N)	N	N	N	Y	N	Y	N	Y
SPI cluster (ave # of SPI cycles in cluster)	-	-	-	2	-	3	-	2
SPI P_{max} (bar)	-	-	-	320	77	280	92	291
SPI P_{ave} (bar)	-	-	-	171	74	157	89	132

Y – yes; N – no; HR – heat release; SPI – stochastic pre-ignition;
 SPIP_{max} – maximum stochastic pre-ignition peak pressure;
 SPIP_{ave} – average stochastic pre-ignition peak pressure

configuration in Figure 4, where results show the modified orientation displayed increased PSHR for a given intake temperature. Moreover, Figure 5 illustrates that the LSPI event severity was significantly increased with the modified orientation. Lastly, Table 2 highlights that in the modified GDI orientation, not only was the LSPI event severity increased, but LSPI events were in the form of “clusters,” which were not observed in the original equipment manufacturer orientation. Based on the results, it is concluded that charge reactivity is critical for LSPI event occurrence, and that fuel–wall interaction is critical for LSPI cluster events occurrence.

Conclusions

The present work has demonstrated that the fundamentals of LSPI are based in fuel and lubricant interactions at high load operating conditions. Results have been disseminated to industry and the community where significant interest was generated. The present work has demonstrated the fundamental operating conditions and regime for LSPI occurrence with common lubricant and fuel properties. Future research directions will probe lubricant properties at the established conditions of interest in an effort to systematically isolate lubricant properties critical to the occurrence of LSPI and improve the fundamental understanding of causes of LSPI.

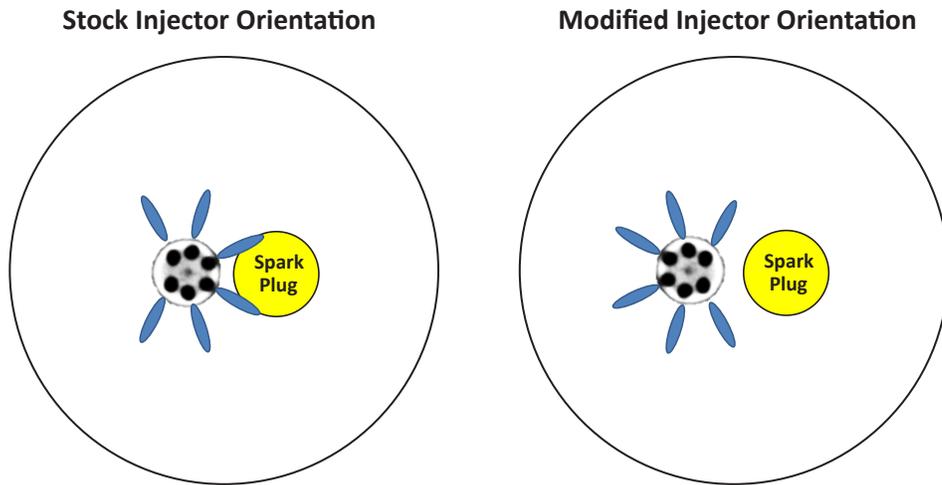


Figure 3. Cartoon depiction of direct injector and spray plume orientation relative to the spark plug and linear wall for stock (left) and modified (right) injector orientations

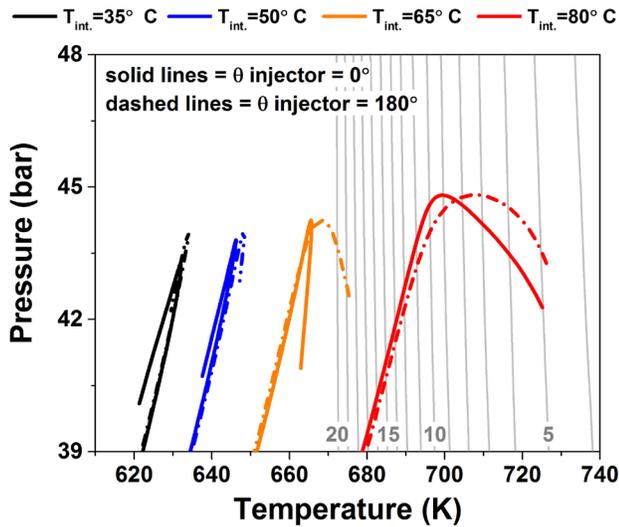


Figure 4. Pressure-temperature trajectory for stock (solid) and modified (dashed) conditions as a function of intake temperature, ΔP is 24 kPa for all cases

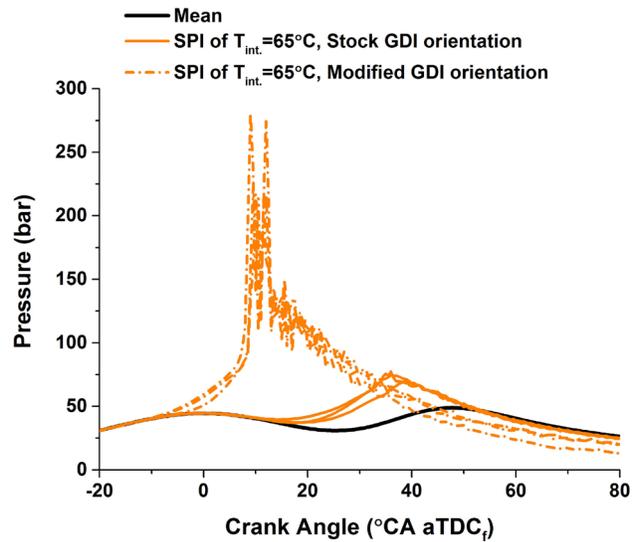


Figure 5. In-cylinder pressure trends of ensemble mean (black), and individual SPI cycles of stock (solid orange) and modified (dashed orange) GDI orientations

Table 2. SPI Tendency of GDI Injector Orientation as a Function of Intake Temperature at Constant Backpressure

ΔP_{engine} (kPa)	24	23	11	24	9	24
T_{intake} (°C)	35	35	35	65	35	80
SPI count (#/30,000 cycles)	0	0	85	3	*	4
SPI cluster (# within 3 cycles)			0	0	*	0
SPI P_{max} (bar)			319	77	*	92
SPI P_{ave} (bar)			119	74	*	89

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), US 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.
5. 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.
6. 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.
7. 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.
8. Dahnz, C, Kyung-Man Han, Ulrich Spicher, Max Magar, Robert Schiefl, and Ulrich Maas. “Investigations on Pre-Ignition in Highly Supercharged SI Engines.” SAE International Journal of Engines 3, no. 1 (2010): 214–224.
9. 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.
10. Szybist, J., and Splitter, D., “Pressure and Temperature Effects on Fuels with Varying Octane Sensitivity at High Load in SI Engines,” In Press. Accepted to Combustion and Flame in November 2016.
11. Splitter, Derek, Barry Burrows, and Sam Lewis. Direct Measurement and Chemical Speciation of Top Ring Zone Liquid During Engine Operation. No. 2015-01-0741. SAE Technical Paper, 2015.

FY 2016 Publications/Presentations

1. West, B et al., “*Lubricant Effects on Combustion, Emissions, and Efficiency*,” DOE Annual Merit Review, Washington, DC, June 2016.
2. Splitter, D., Kaul, B., and Szybist, J., “*An Update of Stochastic Preignition Research at ORNL*,” April 2016, presented to Driven Racing Oil, Charlotte, North Carolina.
3. Splitter, D., Kaul, B., and Szybist, J., “*An Update of Stochastic Preignition Research at ORNL*,” August 2016, presented via web to General Motors Powertrain, Pontiac, Michigan.
4. Splitter, D., Kaul, B., Szybist, J., “*An Update of Stochastic Preignition Research at ORNL*,” August 2016, USCAR, Southfield, Michigan.

V.11 Compatibility of Antiwear Additives with Non-Ferrous Engine Bearing Alloys

Overall Objectives

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 non-ferrous engine bearing alloys, specifically aluminum and bronze alloys that are commonly used in connecting rod end journal bearings and bushings, to gain fundamental understanding to guide future development of engine lubricants.

Fiscal Year (FY) 2016 Objectives

- Investigate the boundary friction and wear behavior of selected Al–Si and bronze alloys in ZDDP- and ionic-liquid-additized lubricants
- Gain initial understanding of the interactions between the AW additives and non-ferrous alloys via tribofilm characterization

FY 2016 Accomplishments

- Conducted a series of boundary lubrication tribo-tests on Al–Si and bronze alloys against steel using ZDDP- and ionic-liquid-additized lubricants
- Friction and wear behavior largely depends on the AW–material combination; Al 380 alloy, ZDDP, phosphate IL, carboxylate IL, and mixture of ZDDP and phosphate or sulfonate IL showed effective wear protection; in contrast, sulfonate IL and mixture of ZDDP and carboxylate IL had a significant detrimental impact with the wear rate increased by two orders of magnitude
- Performed tribofilm morphology examination and composition analysis to seek fundamental understanding of the lubricant–material compatibility

Future Directions

- Continue to explore the effectiveness of AW additives on bronze in boundary lubrication
- Understand the mechanisms behind the detrimental impact observed on some AW additives when lubricating Al–Si and bronze alloys
- Expand the compatibility study to friction modifiers interacting with Al–Si and bronze alloys in mixed and moderate boundary lubrication regimes ■

Jun Qu (Primary Contact) and Yan Zhou

Oak Ridge National Laboratory
Materials Science & Technology Division
P.O. Box 2008
Oak Ridge, TN 37831-6063
Phone: (865) 576-9304
Email: qujn@ornl.gov

DOE Technology Development Manager:
Michael Weismiller

Introduction

Decreasing engine oil viscosity inevitably reduces the thickness of oil films at the engine bearing interfaces, a wear challenge with more frequent surface asperity collisions. Bronze- and aluminum-based alloys are commonly used in connecting rod end journal bearings and bushings. However, current engine lubricants and their additive packages were designed for ferrous alloys and their compatibility with non-ferrous alloys is not well understood. For instance, literature results of using ZDDP-containing oils lubricating aluminum alloys varied significantly in different testing conditions. One study reported effective wear reduction of aluminum in high-load rolling contact when 5% ZDDP was introduced to the oil [1]. In contrast, another report showed that the addition of 5% ZDDP increased the wear rate of an Al alloy sliding against steel [2]. This project investigates the compatibility of engine lubricant AW additives, specifically conventional ZDDP and newly developed ILs, with selected non-ferrous engine bearing alloys, specifically aluminum and bronze alloys. Fundamental understanding gained in this study will help guide future development of engine lubricants.

Approach

Work scope includes: (1) tribosystem analysis of the engine bearing interfaces of interest to design the tribological bench tests, (2) investigation of the boundary friction and wear behavior for selected bronze and Al–Si alloys lubricated by ZDDP- and ionic-liquid-additized lubricants, and (3) understanding the tribochemical interactions between the non-ferrous alloys and AW additives via tribofilm characterization.

As shown in Figure 1, four AW additives were used in our study: a secondary ZDDP, a phosphonium–phosphate IL ($[P_{8888}][DEHP]$, >10% oil solubility), a phosphonium–carboxylate IL ($[P_{66614}][C_{17}H_{35}COO]$, >10 % oil solubility), and a phosphonium–sulfonate IL ($[P_{66614}][RSO_3]$, 1–2% oil solubility). All three ILs had previously shown effective wear protection for ferrous alloys [3]. Each additive was added into a SAE 0W-30 base oil at a treat rate to get a phosphorus content of 800 wt ppm. When two additives were used together, each contributed 400 ppm P. Aluminum alloy 380 and bronze alloy C932 were rubbed against American Iron and Steel Institute 52100 steel bearing balls of 10 mm using a Plint TE77 tribometer. The reciprocating sliding tests were carried out at ambient environment under a 20 N load and a 10 Hz oscillation with a 10-mm stroke for 200 m to 10,000 m sliding. The friction coefficient was captured in situ and wear volume was quantified using white interferometry. The worn surface morphology and composition were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

Results

Investigation of the Compatibility Between AW and Aluminum Alloy

Figure 2a shows the friction behavior of three 1,000-m tests of the steel–aluminum contact in the base oil and the

surface morphology of the steel balls that rubbed against Al 380 flats. The worn surfaces on the steel balls showed clear signs of material transfer from the Al 380 flats. As highlighted in the friction plots, each test started with a period of a higher level of friction (~0.08) and dropped to a lower level (<0.05) with a quick transition. The wear volume of the Al flats in the three tests were 0.082 mm³, 0.12 mm³, and 0.036 mm³, respectively, which seemed proportional to the span of the high-friction stage. A 200-m test was then performed to intentionally stop in the high-friction stage, and its friction trace is shown in Figure 2b. The SEM imaging and EDS elemental mapping indicated an Al- and O-rich transfer layer on the steel counterface. An extended test of 10,000-m sliding was also run, and the friction curve is shown in Figure 2c. The wear volumes for the 200-m test and the 10,000-m test were 0.014 mm³ and 0.022 mm³, respectively, indicating that most material loss occurred in the high-friction stage.

The friction traces of three repeat tests for each oil containing a single AW additive, ZDDP or IL with 800 ppm P content, are shown in Figure 3a. The wear volume of the Al 380 flat in each individual test is marked in the legend. Average wear volumes are compared in Figure 3b. The addition of the ZDDP, phosphate IL or carboxylate IL either eliminated or reduced the length of the high-friction stage and the wear volume.

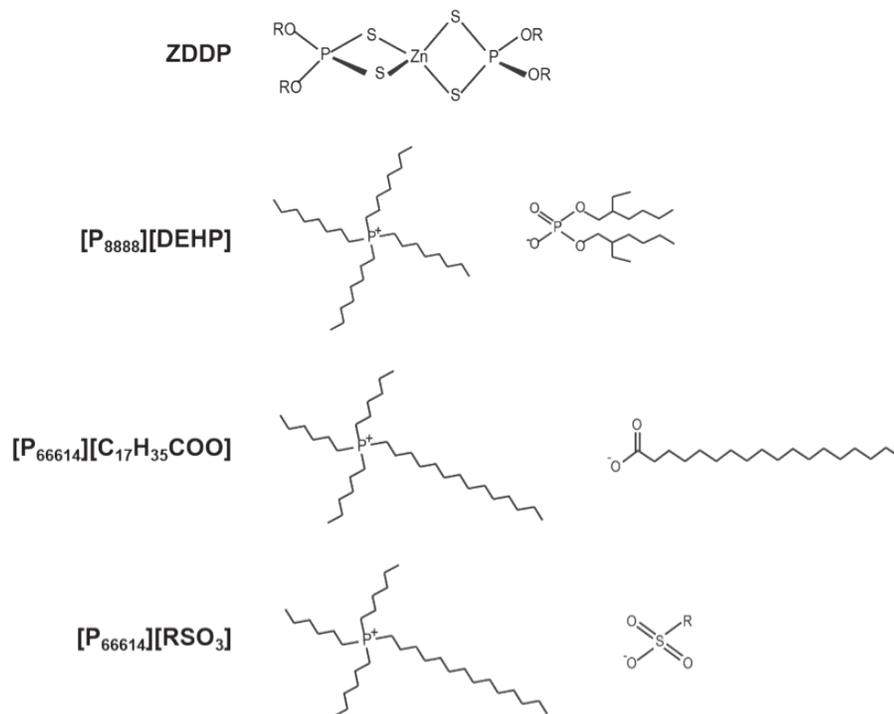


Figure 1. Molecular structures of ZDDP and three ILs used as AW additives in this study.

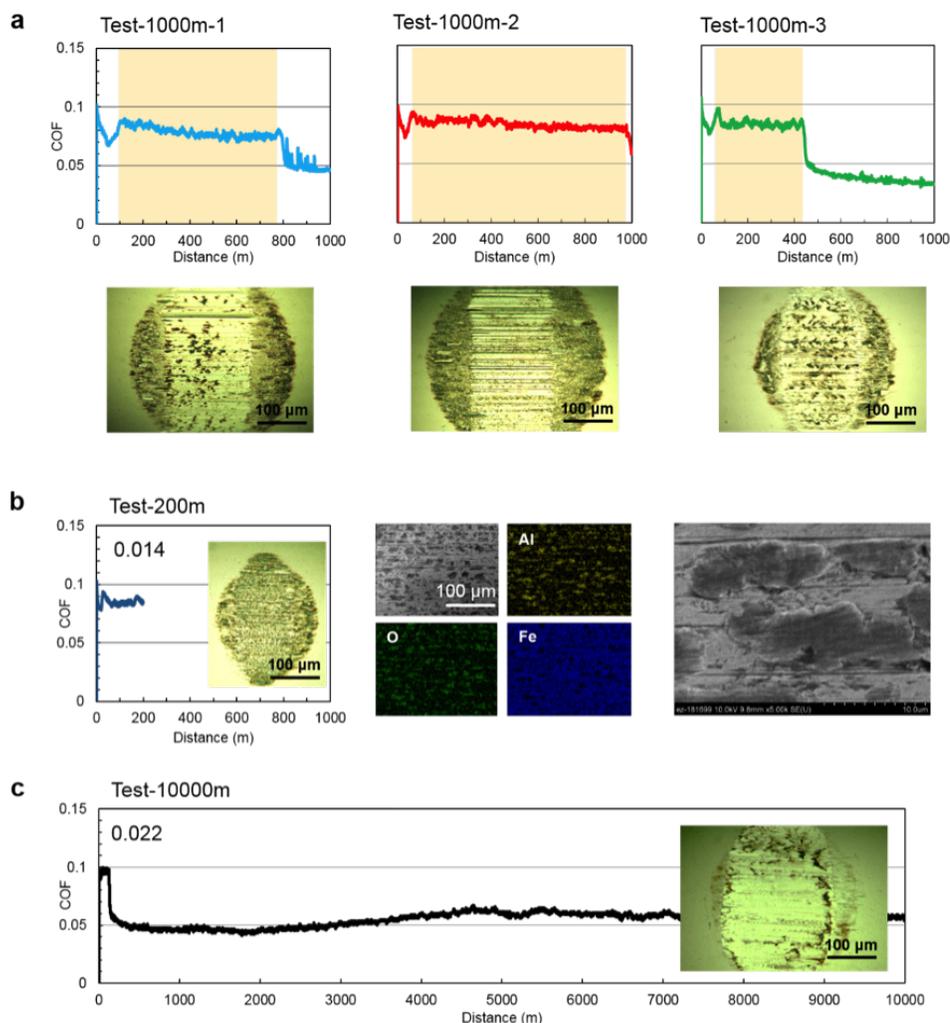


Figure 2. Friction and wear results of the Al 380 alloy flats sliding against 52100 steel balls in the base oil. (a) Coefficient of friction (COF) of 1,000 m sliding tests and the optical images of steel ball wear scars. (b) COF of a 200 m sliding test and the SEM images and EDS maps of the steel ball wear scar suggesting that the transfer film is rich in aluminum and oxygen. (c) COF of a 10,000 m sliding test and an optical image of the steel ball wear scar with little transfer material.

The wear protection on the Al 380 alloy is ranked as ZDDP > carboxylate IL > phosphate IL. In contrast, the sulfonate IL surprisingly caused an increase in friction (steady-state COF around 0.12) and significant material loss ($\sim 5.0 \text{ mm}^3$), much higher than that for the base oil without the sulfonate IL. Figure 3c plots the wear volume of individual tests against the sliding distance of high-friction stage (COF > 0.065), which shows a strong linear correlation.

The sulfonate IL was further investigated because of its wear problem in lubricating Al described above. There was no sign of corrosion on the Al 380 alloy surface after being exposed to the sulfonate IL for two weeks at room temperature or 2 h at 200°C. The sulfonate IL

was then added to the base oil at various concentrations, contributing 200 ppm P, 80 ppm P, and 33 ppm P, respectively. All concentrations behaved similarly and the reduction in concentration did not seem to slow down the material removal rate, as shown in Figure 4. One hypothesis for the detrimental effect is tribocorrosion. Sulfonate IL is known to quickly react with the aluminum surface to form a passive film in static environments [4]. In tribo-contact, however, such a passive layer would be damaged or removed instantaneously by the wear process, which will expose the fresh substrate to trigger new reactions such a mechanochemical process is suspected to cause an increased material removal rate.

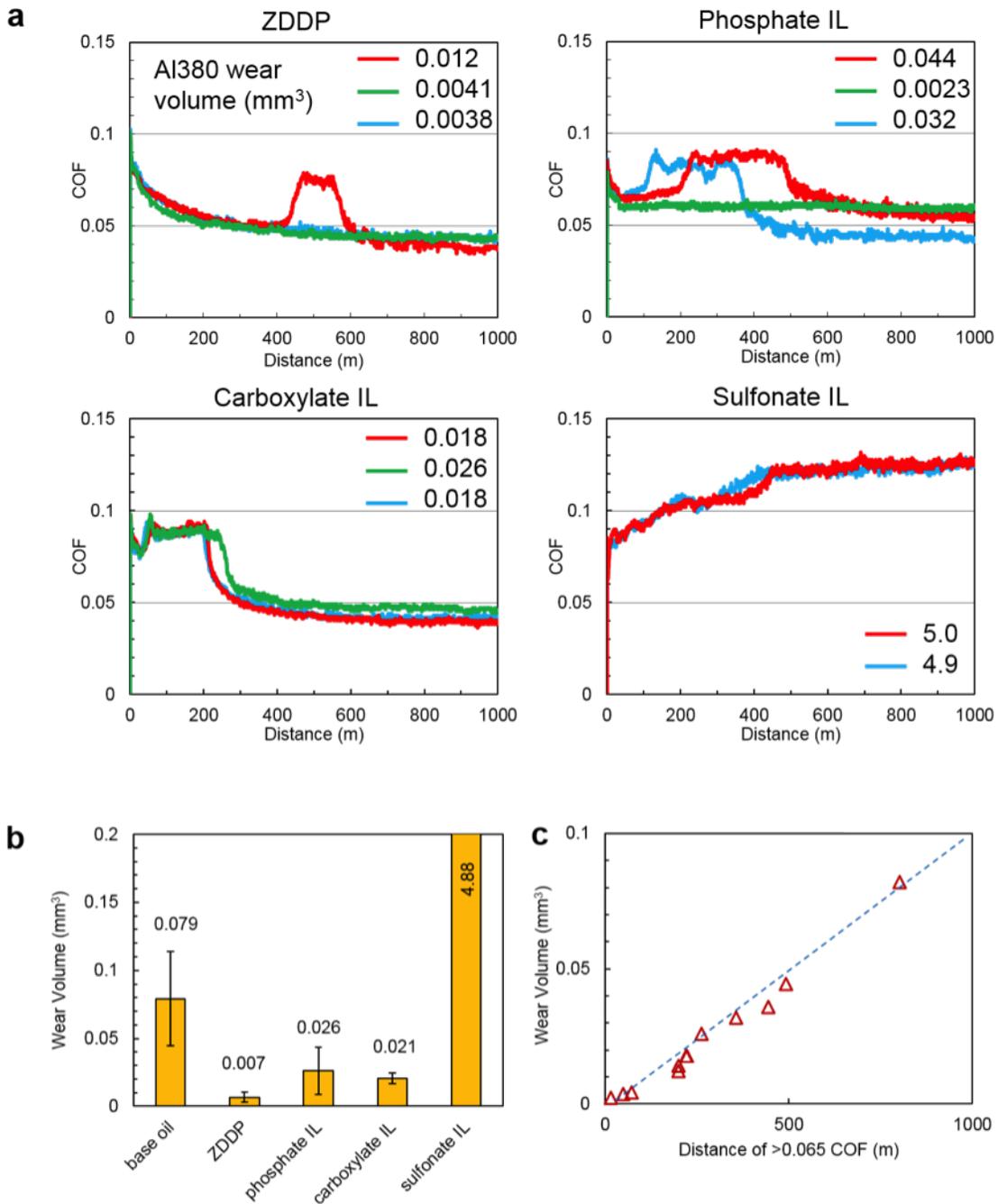


Figure 3. Friction and wear results of the Al 380 alloy flats sliding against 52100 steel ball in the oils containing a ZDDP or IL. (a) Friction behavior of ZDDP, phosphate IL, carboxylate IL, and sulfonate IL at 800 ppm P. Wear volumes were marked in the legend in mm³. (b) Comparison of wear volumes. (c) A plot of the wear volume of individual test vs. the sliding distance for tests having COF > 0.065.

SEM images and EDS spectra of the worn Al 380 surfaces are shown in Figure 5. There were no significant peaks for Zn, P, or S, suggesting the lack of detectable tribofilm formed by either ZDDP or ILs. Further investigation will be carried out by using the surface-sensitive X-ray photoelectron spectroscopy.

Figure 6 shows the friction traces and wear volumes for the combinations of ZDDP+IL (1:1 molecular ratio) at a total 800 ppm P. Interestingly, the detrimental effect of the sulphonate IL was mitigated by the ZDDP when used together. On the other hand, an antagonistic effect was discovered between the ZDDP and carboxylate IL with

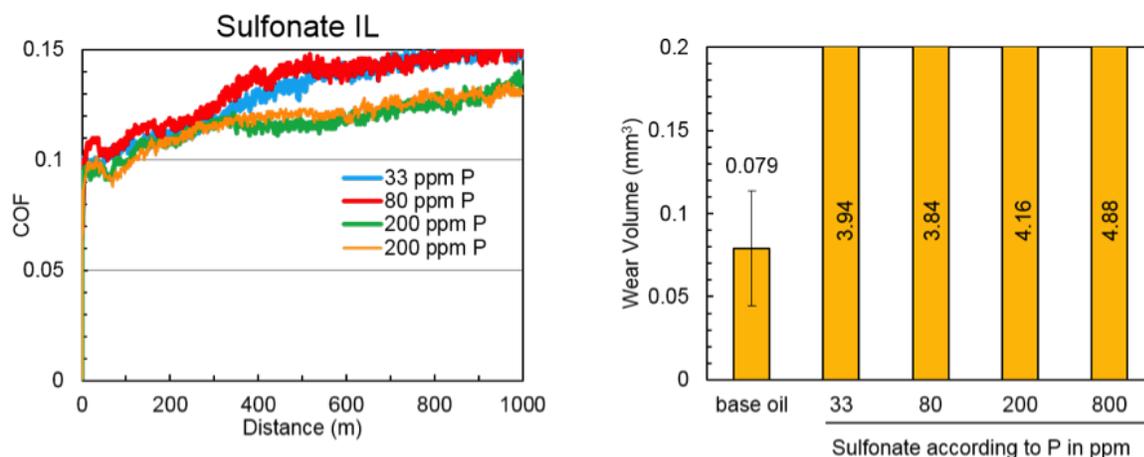


Figure 4. Friction traces and wear volumes of Al 380 alloy flat sliding against 52100 steel ball in the oils containing various amounts of the sulfonate IL with P contents of 200 ppm, 80 ppm, and 33 ppm.

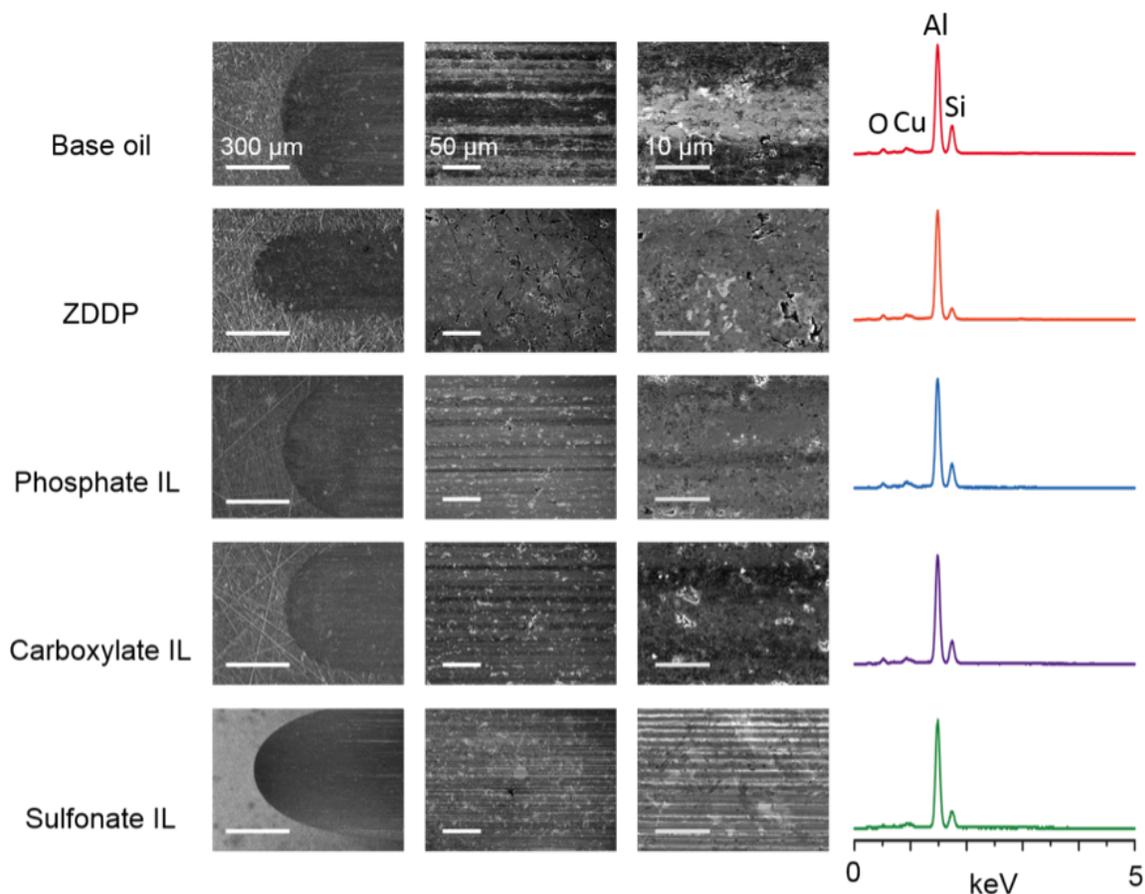


Figure 5. SEM images and EDS spectra of the wear scars on Al 380 alloy flat.

wear rate increased by more than two orders of magnitude compared with using either of them alone. Again, tribocorrosion is a possible explanation. While carboxylic acid alone has little corrosive attack to aluminum, the

combination of carboxylic acid and phosphate has been used for efficient dealumination [5]. This suggests potentially strong chemical reactions with aluminum when the ZDDP and carboxylate IL both are present.

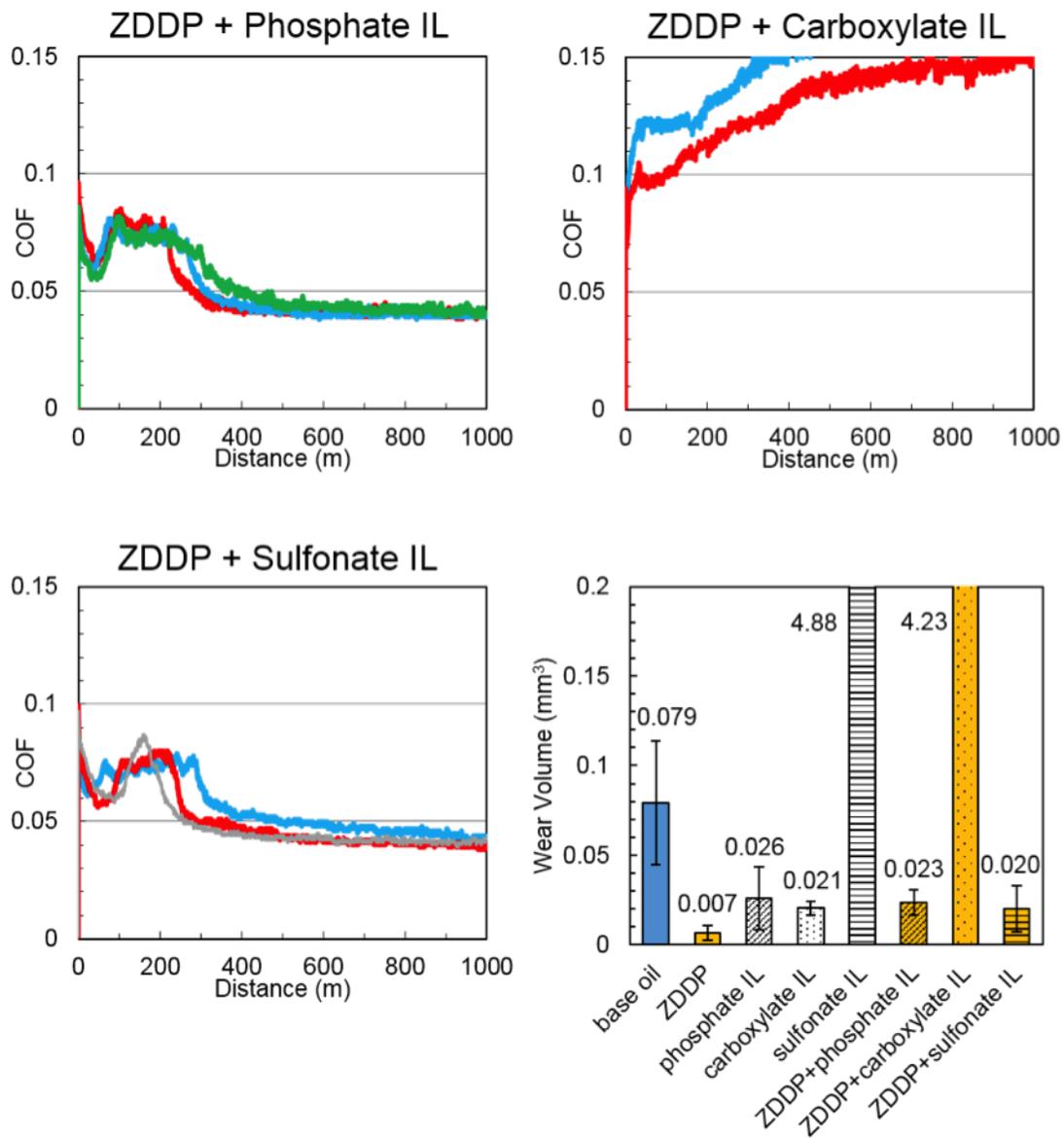


Figure 6. Friction and wear results of the Al 380 alloy flats sliding against 52100 steel ball in the oils containing the ZDDP and an IL at 1:1 molecular ratio with the total P content of 800 ppm.

Investigation of the Compatibility Between AW and Bronze

We have started the study of compatibility between AW additives and bronze. However, initial wear results showed poor repeatability from sample to sample. For the same lubricant, the wear on one bronze sample could be several times higher than that of another bronze sample, whereas all bronze samples were machined from the same plate. Investigation is under way.

Conclusions

A series of boundary lubrication tribo-tests have been conducted on selected Al-Si and bronze alloys against steel using ZDDP- and IL-additized lubricants. The friction and wear behavior varied significantly for different additive chemistry. In lubricating the Al 380 alloy, the addition of ZDDP, phosphate IL, carboxylate IL, ZDDP+phosphate IL or ZDDP+sulfonate IL provided effective wear protection. However, the sulfonate IL and mixture of ZDDP and carboxylate IL had unexpected detrimental impact increasing the wear rate by two orders of magnitude. A tribo-corrosion hypothesis has been

proposed and characterization is being performed to seek fundamental understanding. Investigation is underway for the poor repeatability observed in the tests of the bronze alloy.

References

1. Kawamura, M.; Fujita, K., "Antiwear property of lubricant additives for high silicon aluminum alloy under boundary lubricating conditions," *Wear* 89 (1983), 99–105.
2. Wan, Y.; Cao, L. L.; Xue, Q. J., "Friction and wear characteristics of ZDDP in the sliding of steel against aluminum alloy," *Tribology International* 30 (1997), 767–772.
3. 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 antiwear additives," *Langmuir* 30 (2014) 13301–13311.
4. B. Zhou, Y. Wang, Y. Zuo, "Evolution of the corrosion process of AA 2024-T3 in an alkaline NaCl solution with sodium dodecylbenzenesulfonate and lanthanum chloride inhibitors," *Applied Surface Science* 357 (2015) 735–744.
5. X. Chang, L. He, H. Liang, X. Liu, Z. Yan, "Screening of optimum condition for combined modification of ultra-stable Y zeolites using multi-hydroxyl carboxylic acid and phosphate," *Catalysis Today* 158 (2010) 198–204.

FY 2016 Publications/Presentations

1. J. Qu, "Using ionic liquids as anti-wear additives to lubricate non-metallic surfaces," *20th International Colloquium Tribology*, Stuttgart, Germany, January 12–14, 2016. (Invited)
2. J. Qu, T. Toops, "Ionic liquids as engine lubricant additives, impact on emission control catalysts, and compatibility with coatings," *DOE Vehicle Technologies Program Annual Merit Review*, Washington, D.C., June 6–9, 2016.
3. Y. Zhou, J. Qu, "Investigation of the compatibility between anti-wear additives and non-ferrous bearing alloys," *STLE Tribology Frontiers Conference*, Chicago, November 13–15, 2016.

V.12 Lubricant Effects on Emissions and Emissions Control Devices

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
- Efforts in this task are completed through two subtasks:
 - Lubricant formulation impacts on gasoline direct injection (GDI) particulate emissions
 - Compatibility of ionic liquid (IL) lubricant additives with three-way catalysts (TWCs)
- Specifically, this project investigated: (1) the aging of a TWC with gasoline engine exhaust containing IL lubricant additives, and (2) the impacts of start-stop operation on particulate matter (PM) emissions from a vehicle equipped with a GDI engine.

Fiscal Year (FY) 2016 Objective

- Analyze data from GDI vehicle start-stop experiments finished in FY 2015; start-up transient operation and fuel choices can affect lubricant emissions from GDI engines
- Quantify the impact of IL additives on a TWC at full useful life
- Finish preparation of GDI engine start cart and commence experiments on lubricant viscosity effects on PM emissions

FY 2016 Accomplishments

- Evaluated soot carbon, particle number emissions, and lubricant contributions to PM chemistry from a GDI vehicle operating in start-stop and no start-stop mode over a vehicle drive cycle transient
- Completed aging experiments of TWC with IL lubricant additives
- Finished GDI engine start cart commissioning and started experiments with different viscosity lubricants

Future Directions

- Complete data analysis of lubricant viscosity effects on GDI engine PM emissions

**John M.E. Storey (Primary Contact),
Todd J. Toops, Melanie Moses-DeBusk,
Samuel A. Lewis, D. William Brookshear,
Eric J. Nafziger**

Oak Ridge National Laboratory
National Transportation Research Center
PO Box 2008, MS 6472
Oak Ridge, TN 37831-6472
Phone: (865) 946-1232
Email: storeyjm@ornl.gov

Dae-Kun Kim and Ke Nguyen

Department of Mechanical, Aerospace and
Biomedical Engineering
University of Tennessee
Knoxville, TN 37996

DOE Technology Development Manager:
Michael Weismiller

- Perform additional GDI engine start cart experiments to examine lubricant additive effects on PM emissions ■

Introduction

This task is a part of 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 fuel and lubricant constituents that can impact emissions and emissions control technologies. The efforts are aimed at specifically addressing barriers that have been identified in the Vehicle Technologies Office's Multi-Year Plan:

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

This project examines lubricant effects on emissions controls as well as the lubricant contribution to PM emissions from GDI vehicles. GDI vehicles currently do not have PM aftertreatment, and, because of pending

increased regulation of PM emissions, it is critical to understand the physical and chemical nature of the PM.

Approach

This research brings together targeted, engine-based studies with in-depth characterization of PM, hydrocarbons (HCs), and other emissions to better understand fuel and lubricant effects on emissions and fuel-lubricant interactions with emissions control devices. As part of this task, a mobile start cart, as shown in Figure 1, was constructed to specifically target lubricant effects on cold-start emissions and fuel efficiency. Efforts in this task are completed through two subtasks: compatibility of IL lubricant additives with emissions control systems and lubricant formulation impacts on GDI PM emissions. The results will be discussed independently for each of these sub-tasks.

Results

Ionic Liquid Lubricant Additive Effects on Emissions Control

TWCs were aged with stoichiometric gasoline engine exhaust at a temperature of 700°C using an accelerated aging protocol [1]. In order to simulate the lifetime exposure of the TWC to the lubricant additives, additives



Photo: Colby Earle

Figure 1. Oak Ridge National Laboratory mobile start cart apparatus equipped with a 2013 2.0 L turbocharged GDI engine and dynamometer. The engine is instrumented for cylinder pressure, crank angle, fuel flow, and exhaust air-fuel ratio and includes high-speed data acquisition. It can be set up in the Oak Ridge National Laboratory vehicle laboratory for full-flow dilution emissions sampling.

were added to the engine's fuel supply such that the full useful life (FUL) exposure of the TWC was obtained in 24 h of operation. In addition to the engine-aged TWCs, a TWC aged on a vehicle for FUL was obtained for comparison. Cores were removed from the front section of each TWC and analyzed on a benchflow reactor. Figure 2 shows the temperature of 90% conversion (T_{90}) of fresh and aged TWC-cored samples for NO, CO, and propylene (a representative HC) during the stoichiometric evaluation [1]. The T_{90} for the zinc dialkyl dithiophosphate (ZDDP)-aged TWC increased the most for conversion of each of the pollutants, and was similar to the field-aged catalyst (FUL). In each case the FUL-aged sample showed similar reactivity as the ZDDP case, suggesting that the accelerated aging approach captures the key deactivation chemistry in a vehicle. The IL and ZDDP+IL aged TWCs showed less of an effect on conversion temperature, suggesting that there would be no harm done to the emissions control through the use of IL lubricant additives.

Lubricant Effects on GDI PM Emissions

Many manufacturers are implementing start-stop operation to enhance vehicle fuel economy by as much as 10%. During start-stop operation, the engine shuts off when the vehicle is stationary for more than a few seconds. When the brake is released by the driver, the engine restarts, and this transient start-up behavior can result in higher PM emissions. The experimental approach was designed to characterize both the effects of gasoline-alcohol blends and lubricants on GDI PM during start-stop transients. The fuels used were gasoline (E0), 20% ethanol in gasoline (E20), and 12% isobutanol in gasoline (iBu12). Figure 3 shows the differences in PM emissions between the cold-start portion of the drive cycle and the hot-start portion of the drive cycle for the different fuels.

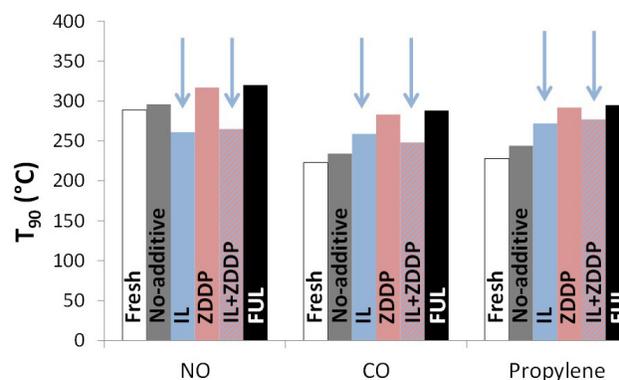


Figure 2. Temperature of 90% conversion (T_{90}) under stoichiometric conditions for NO, CO, and propylene for six different catalysts: fresh; then aged with no additive, IL, ZDDP, IL+ZDDP; and then vehicle aged for FUL

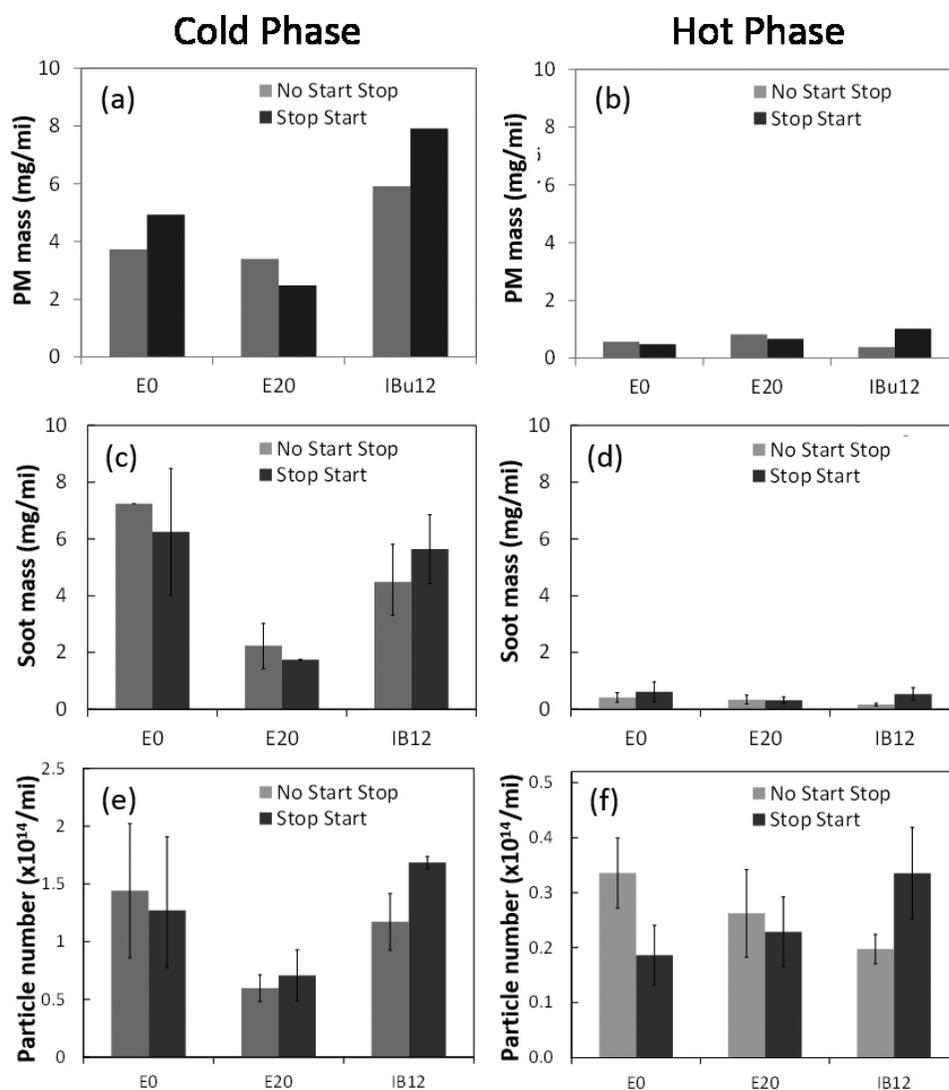


Figure 3. Comparison of hot and cold stop-start emissions

The cold phase results in higher mass, soot carbon, and particle number emissions than the hot phase. During the cold phase, E20 results in the lowest emissions in all three cases (Figures 3a, 3c, 3e). During the hot phase, the results are less straightforward and the fuels which had the lowest emissions are shown in Table 1. Although the cold phase has higher emissions for all fuels, the hot phase represents the majority of vehicle operation time. Analysis of variance was carried out on 27 hot phase cycles and a statistically significant difference in the soot mass emissions was observed between fuels, and between operating modes (start-stop operation vs. no start-stop operation). For particle number emissions, a statistically significant difference was not seen between fuels or between operation modes. However, a statistically significant difference was seen for both soot mass and particle number emissions when the combined impact of both fuel effects and operating mode effects on emissions

Table 1. Fuels that Resulted in the Lowest GDI Vehicle Emissions Rates for PM Mass, PM Soot, and Particle Number During Hot Phase Operation for Both Start-Stop and No Start-Stop Operation

Lowest value:	No Start-Stop	Start-Stop
PM Mass	E0 ~ E20	E20
Soot Mass	iBu12	E0
Particle #	iBu12	E0

were considered, (i.e. the interaction between fuel and mode).

In order to determine the lubricant contribution to the PM, PM was collected over multiple cold cycles (three), and hot cycles (up to 27). The PM was then harvested from

the sample filters and analyzed by gas chromatography–mass spectroscopy using a technique developed by Oak Ridge National Laboratory [2]. Figure 4 shows representative chromatograms of the soot HCs for both cold and hot phases. As indicated in Figure 4, the shaded section illustrates where the lubricant HCs would appear in the chromatogram if they were present. Because excess fuel is typically injected to initiate the start, the first fuel spray can penetrate to the walls of the cylinder and liberate lubricant into the cylinder. Thus the lack of lubricant HC contribution to PM emissions from start-stop operation is a significant finding.

Conclusions

- Novel IL lubricant additive has less impact on the catalytic activities of the TWC than the industry standard ZDDP.
- Ethanol–gasoline blends can lower cold phase PM mass, soot, and number emissions.
- Warmed-up start-stop operation does not necessarily increase PM emissions, and the lubricant does not appear to be present in the PM.

References

1. Xie, C.T., T.J.; Lance, M.J.; Qu, J.; Viola, M.B.; Lewis, S.A.; Leonard, D.N.; Hagaman, E.W, *Catalysts* 6: 2016.
2. Storey, J.M.; Lewis, S.A.; Szybist, J.; Thomas, J.; Barone, T. Eibl, M.; Nafziger, E.; Kaul, B. *SAE Int. J. Fuels Lubr.* 7 (2): 2014.

FY 2016 Publications/Presentations

1. Xie, C.T., T.J.; Lance, M.J.; Qu, J.; Viola, M.B.; Lewis, S.A.; Leonard, D.N.; Hagaman, E.W, *Catalysts* 6: 2016.
2. Kim, D-K.; Nguyen, K.; Brookshear, D.W.; Toops, T.J. “Impact of lubricant oil additives on the performance of Pd-based three-way catalysts,” abstract *accepted* for presentation at the North American Catalysis Meeting 2017.

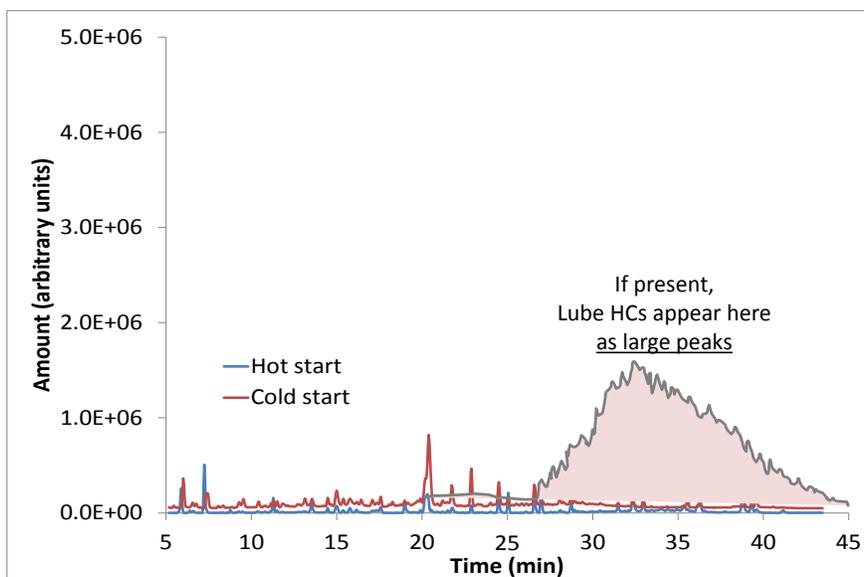


Figure 4. Gas chromatography–mass spectroscopy comparison of hot- and cold-start HC speciation

V.13 ORNL–GM: Development of Ionic Liquid-Additized, GF-5/6 Compatible Low-Viscosity Oils for Automotive Engine and Rear Axle Lubrication for 4% Improved Fuel Economy

Overall Objectives

- Further develop ionic liquid (IL)-additized low-viscosity engine oils meeting the GF-5/6 specifications and possessing superior lubricating characteristics
- Expand the IL additive technology to rear axle lubricants
- Seek a combined improvement in the vehicle fuel economy

Fiscal Year (FY) 2016 Objectives

- Identify the best candidate IL+zinc dialkyldithiophosphate (ZDDP) combination and the optimal treat rate
- Demonstrate >50% wear reduction for the IL+ZDDP combination compared with ZDDP alone at the same phosphorus level in bench tests
- Investigate the potential impact of a candidate IL+ZDDP combination on three-way catalysts (TWCs)

FY 2016 Accomplishments

- We submitted two journal papers and gave two invited talks at technical conferences.
- A phosphorus-containing IL has been identified to have the best synergistic effects with ZDDP when used at 1:1 molecular ratio. When combining the IL with a secondary ZDDP, the optimal treat rate was found to have the P content of 400–800 ppm, which well overlaps with the 600–800 ppm regulated by the GF-5/6 specifications.
- More than 50% wear reduction was demonstrated by the IL+ZDDP combination compared with the ZDDP alone when added to a polyalphaolefin 4 cSt base oil at the P level of 800 ppm when tested in boundary lubrication at 150°C.
- The potential impact of the IL+primary ZDDP combination on TWCs has been investigated. The adverse impact seemed to be minimal.
- A rolling-sliding contact fatigue bench test is being designed to simulate the lifetime heavy-duty cycles

Jun Qu (Primary Contact), Yan Zhou, Huimin Luo, Todd Toops, Daniel W. Brookshear, and Benjamin Stump

Oak Ridge National Laboratory (ORNL)
P.O. Box 2008, MS-6063
Oak Ridge, TN 37831-6063
Phone: (865) 964-3025
Email: qujn@ornl.gov

Michael Viola, Khaled Zreik, and Tasfia Ahmed

General Motors (GM) Research and Development Center
800 N. Glenwood Ave.
Pontiac, MI 48340-2925
Phone: (586) 243-2397
Email: michael.b.viola@gm.com

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

based on contact mechanics and lubrication modeling of the rear axle key contact interface.

Future Directions

- Formulate a new prototype GF-5/6 SAE 0W-12 engine oil using the top-performing IL+ZDDP combination as the antiwear additive
- Conduct tribological bench tests and engine dynamometer tests to evaluate the improvement on wear protection and fuel economy
- Develop an IL-additized low-viscosity rear axle fluid and demonstrate improved durability and efficiency ■

Introduction

For an automotive vehicle, 10–12% fuel energy is lost to the parasitic friction in the engine and another 3–5% must overcome the friction in the rear axle [1,2]. The automotive industry has been applying increasingly lower viscosity oils for both the engine and rear axle to improve fuel economy. The concern in further viscosity reduction is accelerated wear due to thinner lubricant films. Developing more effective anti-wear additives to allow the use of lower viscosity oils has proven to be the most successful and cost effective route. Based on our previous success [3–5] in developing oil-soluble ILs as lubricant additives, the ORNL–GM team is committed in this joint effort to further develop the ILs lubrication technology for both the engine and rear axle to gain a combined improvement in the vehicle fuel economy.

Approach

Work scope includes: (1) further development of IL-additized low-viscosity engine oils meeting the International Lubricants Standardization and Approval Committee GF-5/6 specifications [6], specifically, investigating the synergy between IL and ZDDP and seeking the optimal treat rate, evaluating the impact of IL+ZDDP on TWCs, formulating a prototype GF-5/6 IL-additized multi-grade low-viscosity engine oil, conducting tribological bench tests and analyses, and performing multi-cylinder engine dynamometer tests; (2) development of IL-additized low-viscosity rear axle lubricants, with efforts focused on establishing a contact fatigue bench test to simulate the lifetime duty cycles of rear axle lubrication, tailoring IL chemistry, formulating a prototype IL-additized rear axle fluid, and conducting bench tests and analyses; and (3) executing vehicle tests to demonstrate the improved fuel economy.

Results

The ORNL–GM team kicked off this joint project on August 4, 2015, and substantial progress has been made in the first year with all milestones met in a timely manner. Based on findings in previous projects, several candidate groups of phosphorus-, sulfur-, or boron-containing ILs have been synthesized. By comparing the physicochemical and tribological properties, a phosphonium-based IL has been identified as the top candidate because of its high oil-solubility, high thermal stability, and synergistic effects with ZDDP in wear protection and friction reduction.

In order to determine the optimal IL:ZDDP ratio, IL+ZDDP combinations with three molecular ratios, 1:2, 1:1, and 2:1, were added to a polyalphaolefin (PAO)

4 cSt base oil for tribological bench testing. Tests were conducted using an American Iron and Steel Institute 52100 steel ball rubbing against a CL35 cast iron flat at 150°C under 100 N load and 10 Hz oscillation of 10-mm stroke for 1,000 m sliding. All IL+ZDDP combinations effectively reduced wear by one order of magnitude compared with the neat base oil, and the 1:1 mix of IL+ZDDP was the best performer with additional 70% wear reduction compared with using the ZDDP alone, as shown in Figure 1.

Further investigation on the 1:1 mix of IL+ZDDP in the PAO base oil was then conducted with two types of ZDDPs, primary and secondary, in a wide range of treat rates to understand the trends of the friction and wear behavior. Results are summarized in Figure 2. The coefficient of friction and wear rate (average of two to three repeat tests) are plotted against the P content in the oil. For IL+secondary ZDDP, the P content of 400–800 ppm seems to have the optimum wear protection (see Figure 2a), which well overlaps with the 600–800 ppm P content regulated by the GF-5/6 specifications. Selected scanning electron microscope images and energy-dispersive X-ray spectroscopy spectra of the worn wears are shown in Figure 3. The morphology and composition of the tribofilm formed in the oil with 400 ppm or 800 ppm of P seem to be distinct from those produced in other concentrations either higher or lower. Particularly, more Zn and P but less S were detected in the tribofilms with better wear performance. For IL+primary ZDDP, the P content of 800–1,600 ppm seems to perform the best, as shown in Figure 2b. This shift in the optimal concentration may be attributed to the lower reactivity of the primary ZDDP compared with the secondary ZDDP.

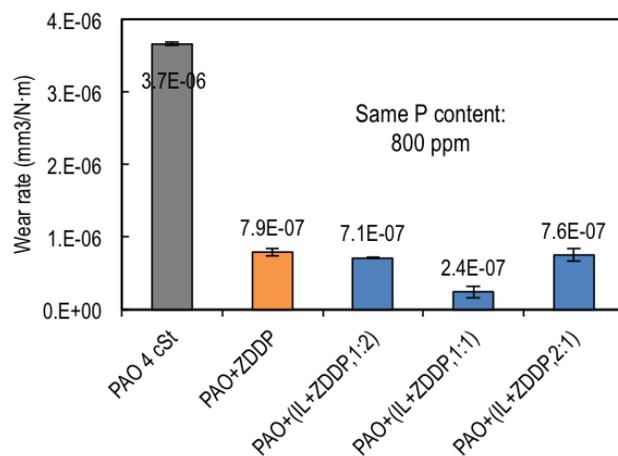
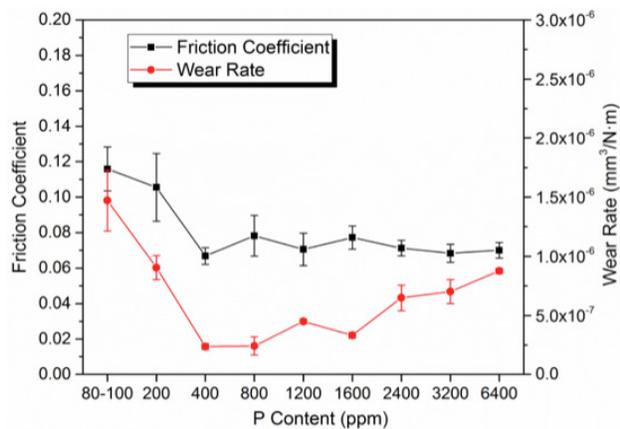
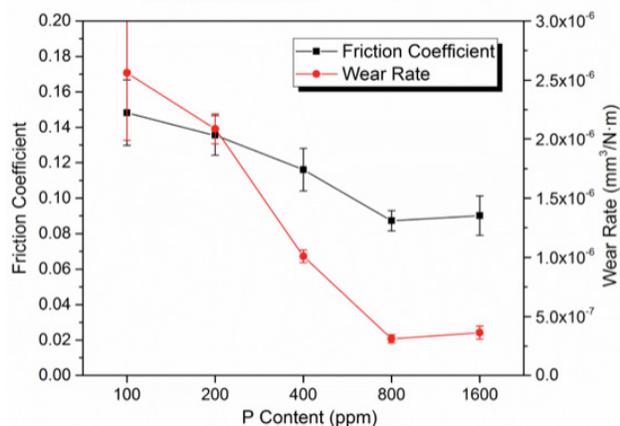


Figure 1. Wear rates using IL+ZDDP combinations of different molecular ratios as oil additives compared with that of the ZDDP alone at the same phosphorus content.



(a) IL+secondary ZDDP [1:1 ratio]



(a) IL+primary ZDDP [1:1 ratio]

Figure 2. Friction and wear results of IL+ZDDP combinations when mixed into a PAO 4 cSt base oil at different concentrations. 400–800 ppm and 800–1,600 ppm of P provided the best wear protection for IL+secondary ZDDP and IL+primary ZDDP, respectively.

Stribeck curve multi-scans were conducted using a Mini Traction Machine. The curves were generated in two lubricants containing ZDDP and IL, respectively, at the same amount of P (800 ppm), under 75 N at 100°C with a 100% sliding rolling ratio (200% for pure sliding). As compared in Figure 4, the Stribeck curve of the ZDDP-additized oil shifted higher from the first to the fourth scan and then stabilized. The increase in friction was associated with the formation of a ZDDP tribofilm that is known to be a rough and high-friction film. In contrast, the Stribeck curve of the IL-additized oil started 30% lower compared to that of the ZDDP-additized oil in the first scan and had little friction increase over the following 19 scans. By the end of the 20 scan tests, the Stribeck curve of the IL-additized oil had a substantial friction reduction by as much as 60% compared to the ZDDP-additized oil. In similar tests, various IL+ZDDP

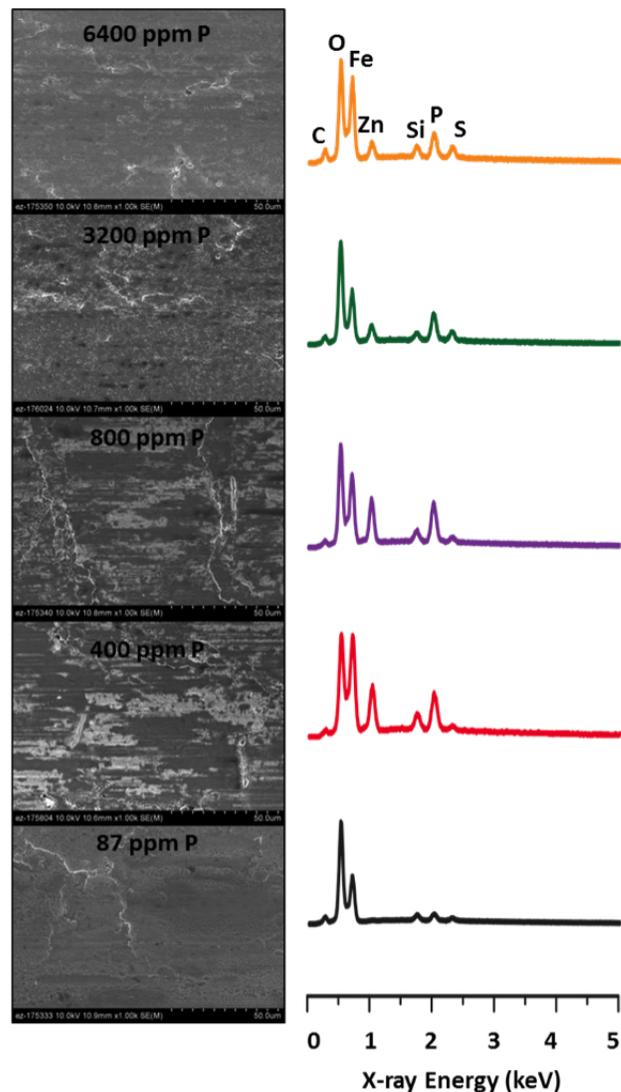
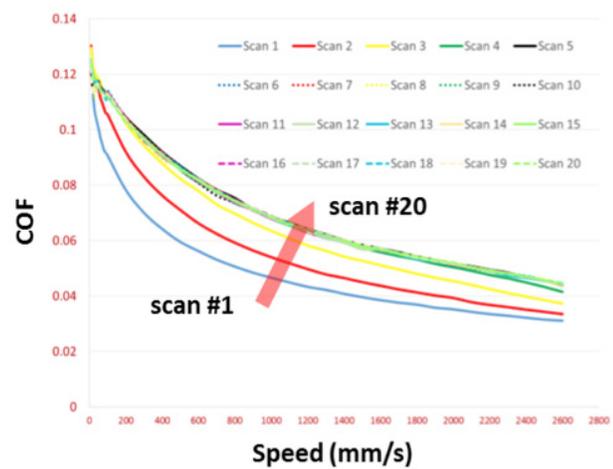


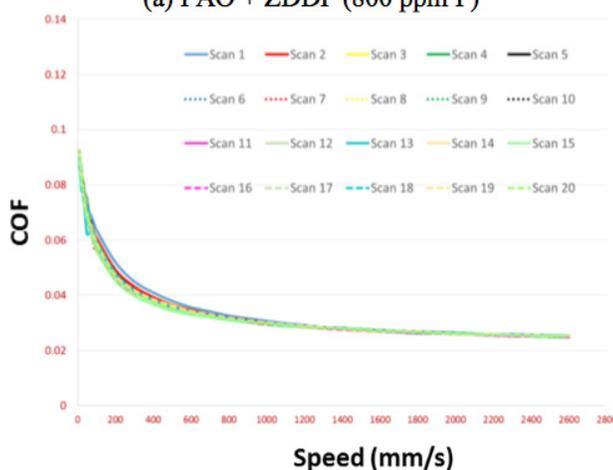
Figure 3. Scanning electron microscopy images and energy-dispersive X-ray spectroscopy spectra of the worn surface of the cast iron flats lubricated by PAO containing various concentrations of IL+secondary ZDDP (the scale bar represents 20 μm).

combinations also produced lower boundary and mixed friction compared with the ZDDP alone.

The impact of IL+secondary ZDDP on TWCs had been revealed in our previous work [7]. This study investigated the effect of the IL+primary ZDDP combination on TWCs using a similar approach based on accelerated small engine testing. Tests using a fresh 2009 Jeep Liberty TWC were compared among no additive, primary ZDDP, IL, and IL+primary ZDDP. Additive introduction was performed using a stoichiometric gasoline genset with the additive mixed with the fuel. Cores from the front 25 mm of the TWCs were removed and evaluated in



(a) PAO + ZDDP (800 ppm P)



(b) PAO + IL (800 ppm P)

COF – coefficient of friction

Figure 4. Stribeck curves of 20 scans for the PAO 4 cSt base oil containing ZDDP or IL, at the same phosphorous content. The IL generated a 30% lower friction in the first scan and 30–60% lower friction in the final scan compared to the ZDDP.

flow reactors. A simulated exhaust mixture containing $\text{CO}/\text{NO}_x/\text{C}_3\text{H}_6$ (propylene)/ C_3H_8 (propane) and a stoichiometric concentration of O_2 was introduced to the catalyst cores in the flow reactor and the temperature was ramped from 100°C to 600°C while measuring the effluent gases. The temperatures of 50% (T50) and 90% (T90) conversion are shown in Figure 5. In general, the reactivity was similar for all of the TWCs tested with the three additives. It should be noted that these evaluations are performed after removing the soot and sulfur from the TWCs, and thus are designed to highlight the impact of the additives. Results suggested that the selected IL+secondary ZDDP combination had minimal adverse impact on TWCs.

A pair of rear axle pinion and ring has been ordered and received from a GM supplier, as shown in Figure 6. Both components are made of carburization case-hardened steel with a manganese–phosphate surface coating. Based on a duty cycle load and speed data from GM, the Hertzian contact stress and lubrication regime (lambda ratio, based on Hamrock and Dowson’s formula) have been determined for each given operation condition. We are developing a bench test using a micropitting rig to simulate the lifetime heavy-duty cycles experienced by the actual rear axles in a vehicle with matched profiles of contact stresses and lubrication regimes. Initial tests have demonstrated the ability of reproducing the typical micropitting damage (see Figure 6) and distinguishing lubricants in surface protection.

Conclusions

Significant progress has been made in the first year of the joint project between ORNL and GM. A top-performing candidate IL has been identified and the optimal molecular ratio mixing with ZDDP was determined to be 1:1. The treat rate with maximum friction and wear reductions for IL+secondary ZDDP were found to be in the range of 0.46–0.92 wt%, or 400–800 ppm P, meeting the 800 ppm maximum specified by the GF-5/6. The IL+ZDDP combination has demonstrated >50% wear reduction compared with the ZDDP alone when added to a low-viscosity base oil at the P content of 800 ppm in boundary lubrication. The adverse impact of the IL+primary ZDDP combination on TWCs seemed to be minimal. In addition to engine lubrication, the exploration of potential application of ILs in rear axle lubrication has started with a rolling–sliding contact fatigue bench test to simulate the lifetime heavy-duty cycles of the actual rear axle.

References

1. S.C. Tung, M.L. McMillan, “Automotive tribology overview of current advances and challenges for the future,” *Tribology International* 37 (2004) 517–536.
2. K. Holmberg, P. Andersson, A. Erdemir, “Global energy consumption due to friction in passenger cars,” *Tribology International* 47 (2012) 221–234.
3. J. Qu, D.G. Bansal, B. Yu, J. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Anti-wear performance and mechanism of an oil-miscible ionic liquid as a lubricant additive,” *ACS Applied Materials & Interfaces* 4 (2012) 997–1002.
4. J. Qu, H. Luo, M. Chi, C. Ma, P.J. Blau, S. Dai, M.B. Viola, “Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive,” *Tribology International* 71 (2014) 88–97.

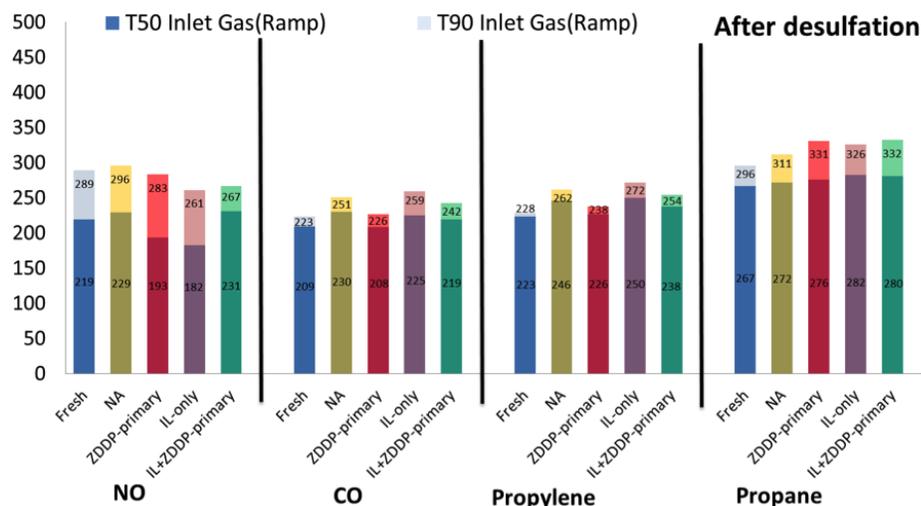
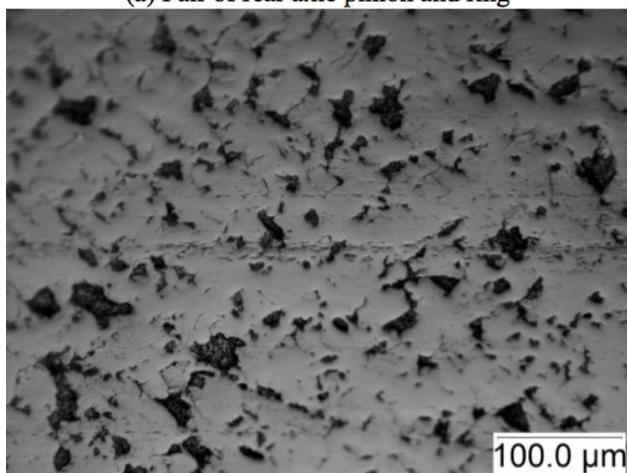


Figure 5. Impact of the primary ZDDP, IL, and IL+primary ZDDP on the TWC (T50 and T90) seemed to be minimal compared to the fresh and no additive (NA) samples.



(a) Pair of rear axle pinion and ring



(b) Micro-pitting produced in the bench test

Figure 6. Pair of rear axle pinion and ring and micro-pitting (typical surface damage of axle) produced in the bench test.

- 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.
- ILSAC Oil Specifications <http://www.oilspecifications.org/ilsac.php>
- C. Xie, T. Toops, M. Lance, J. Qu, M. Viola, S. Lewis, D. Leonard, E. Hagaman, “Impact of lubricant additives on the physicochemical properties and activity of three way catalysts,” *Catalysts* 6 (2016) 54.

FY 2016 Publications/Presentations

- C. Xie, T. Toops, M. Lance, J. Qu, M. Viola, S. Lewis, D. Leonard, E. Hagaman, “Impact of lubricant additives on the physicochemical properties and activity of three way catalysts,” *Catalysts* 6 (2016) 54.
- Y. Zhou, J. Qu, “Ionic liquids as lubricant additives – a review,” *ACS Applied Materials & Interfaces* (in press).
- J. Qu, “Ionic liquids as novel lubricant additives and their compatibility with other lubricant additives and non-ferrous materials,” *2016 Tribology Gordon Research Conference*, Lewiston, ME, June 26–July 1, 2016. (Invited)
- J. Qu, “Oil-miscible ionic liquids as multi-functional additives for low-viscosity engine lubricants,” *20th International Colloquium Tribology*, Stuttgart, Germany, January 12–14, 2016. (Invited)

V.14 High Efficiency Lubricant Oils and Additives Research

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 and 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 viscosity index improvers as a follow on work from the funding opportunity announcement (FOA) project
- Conduct fundamental research to support the awarded FOA 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) 2016 Objectives

- Synthesize and tribology characterize several polar base oils with good viscosity indexes, which are miscible with petroleum-based oils, such as a Group III oil
- Evaluate size changes of various polymeric architectures as they pertain to viscosity index changes, via molecular dynamics (MD) simulations
- Continue dynamic light scattering (DLS) and small-angle neutron scattering (SANS) studies of various viscosity index improver (VII) architectures
- Publish one manuscript that captures the DLS, SANS, and MD simulations work
- Demonstrate shear stability improvements in hyperbranched polymer structures designed as VIIIs
- Investigate shear thinning simulations to build a predictive model spanning various architectures and topologies

FY 2016 Accomplishments

- Completed the study of temperature-induced conformational and size changes using simulations, DLS, and SANS
- Fundamental study led to the publication of a manuscript that captures all the technical details and complexity of the work

**Lelia Cosimbescu (Primary Contact),
Priyanka Bhattacharya, Robert Erck,
Susan Krueger, Ashlie Martini,
Uma Shantini Ramasamy,
Joshua Robinson, Barbara Tarasevich.**

Pacific Northwest National Laboratory (PNNL)
PO Box 999
Richland, WA 99352
Phone: (509) 375-6478
Email: lelia.cosimbescu@pnnl.gov

DOE Technology Development Manager:
Michael Weismiller

Information Release #PNNL-26104

Subcontractors:

- Ashlie Martini and Uma Shantini Ramasamy, University of California, Merced, Merced, CA
- Robert Erck, Argonne National Laboratory (ANL), Lemont, IL

- Achieved the scale-up of three polar base oils and established tribological characterization path with ANL collaborators
- Demonstrated an increase in shear stability of 50–100% in certain hyperbranched polymers versus benchmark materials
- Demonstrated the value of modeling in predicting viscosity changes with temperature of viscosity modifiers

Future Directions

- Finish the synthesis and evaluation of the hyperbranched polymers targeted for shear stability, to enable publishing in a peer reviewed journal
- Investigate the tribological behavior of PNNL base oils in collaboration with ANL scientist, to leverage our individual expertise
- Publish work generated in collaboration with ANL ■

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); achieving a fundamental understanding of viscosity modifiers by probing for temperature-dependent molecular changes via modeling, DLS and SANS (Task 2); developing a molecular design to enhance the shear stability of VIIs (Task 3); and continue to explore the application of MD simulations for the advancement of both VII and base oils (Task 4).

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. 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, particularly friction reducing properties.

Task 2

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 temperature-induced changes at the molecular level, DLS, SANS, and modeling will be applied to study such events.

Task 3

Shear thinning is a known problem with VIIs, and the larger the molecules are, the larger the undesirable effect. One way to circumvent this mechanical phenomenon is to increase the number of arms, such as in a hyperbranched architecture. In this task, we are probing the effect of the degree of hyperbranching in poly(alkyl methacrylate)-based polymers on shear stability.

Task 4

The University of California, Merced team has continued to use MD simulations to study the shear thinning and temperature response of VIIs and base oils. The VII chemistries explored this year include olefin co-polymers,

poly(alkyl methacrylate), highly branched polyethylene, star poly(dodecyl methacrylate), styrene butadiene, and polyisobutylene. Base fluids studied include trimethylololate and triazine.

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. Our research focused on the synthesis of amide or amine-containing analogues. Nitrogen-containing additives have enhanced interactions with surfaces, and could offer an added advantage to polyesters.

Task 2

Proof of concept measurements were 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 allowed (DLS, SANS). Data that clearly suggests a change in size indicative of thermoresponsive behavior is considered a positive result. The conventional belief is that polymers expand with temperature, from a collapsed coil conformation. This study is set to study this mechanism at molecular level.

Task 3

Expertise gained from the FOA project was used for this task to build polymers with hyperbranched cores and polymethacrylate arms. Several polymers were synthesized, characterized, and their viscosity profile and shear stability evaluated. These highly branched architecture are expected to have enhanced shear stability versus their linear or moderately branched counterparts. The potential influence of cores towards viscosity modification and shear stability was studied.

Task 4

Simulations were used to characterize the viscous performance of the base fluids as a function of shear rate and temperature. To understand these trends, we also characterized molecular-scale features in the model, including inter- and intra-molecular interactions. In simulations with VIIs, the radius of gyration of the molecules was calculated from the mass weighted average distance from the center of mass of the molecule to each atom in the molecule.

Table 1. Viscosity Measurements of Oleate Ester (20R) and Triazine Analogues (39R and 45)

Sample ID	KV40 (cp)	KV100 (cp)	VI	Pour point (°C)
61828-20R	39.3	8.7	215	-48
61828-39R	21.9	5.4	214	-12
61828-45	46.3	7.01	108	n/a

KV40 – kinematic viscosity at 40°C; KV100 – kinematic viscosity at 100°C; n/a – not available

Results

Task 1

Of the various base fluids synthesized, only three were selected for further evaluation, specifically those which were easily synthesized or provided a high viscosity index (VI). The three materials are presented in Table 1.

Although Analogue 45 has a low VI, it was used as a comparative example to Analogue 39R, both having the same hexahydrotriazine core. The friction and wear of the three oils were measured at 25°C and 100°C, by our ANL collaborators and shown in Figure 1.

Coefficient of friction for 20R, the oleate ester oil, was steady and about 0.07–0.08 for duration of test at both RT and at 100°C. However the coefficient of friction for 39R oil was high at 100°C (0.13 max) and smaller at RT (0.085–0.09 constant) and similarly, the coefficient of friction for 45 oil tended upward for 100°C (0.12) tests but smaller and steady at RT (0.085–0.1). Based on the friction results, it is expected that the ester will produce little if any wear, while the triazines will produce significant wear. The results, together with friction and wear of conventional base oils (both additized and additive free) will be reported in a future report.

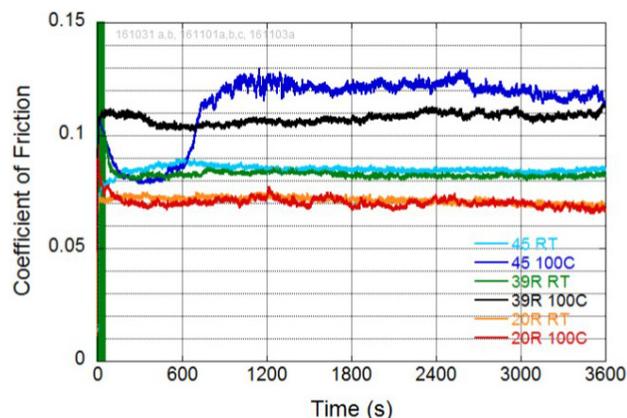


Figure 1. Friction results for three base fluids at room temperature (RT) and 100°C

Task 2

The approach and results on this task are reported in detail in a published paper [1].

Task 3

A core-first strategy was employed to prepare multi-arm stars from hyper-branched cores which were subsequently utilized as a head group for atom transfer radical polymerization. These cores were selected because of their commercial availability, moderate molecular weights, comparable architectures, and differing chemical compositions to explore the potential influence of cores towards viscosity modification and shear stability. The post-modification as well as polymerizations were verified by standard nuclear magnetic resonance spectroscopy and size exclusion chromatography. Estimated conversions (monomer into polymer; percent) and chemical compositions were determined by nuclear magnetic resonance, whereas relative molecular weights, as compared to poly(methyl methacrylate) standards, were acquired by size exclusion.

The polymeric analogues were blended initially at 2% w/w and 5% w/w concentrations in a Group III oil, Yubase 4. Their dynamic viscosities (DV) were measured by a Brookfield viscometer at 10°C, 25°C, 40°C, 60°C, and 100°C. Table 2 includes this data for the 5% w/w blends with the calculated kinematic viscosities (KV) at 40°C and 100°C. These numbers were utilized to generate VI values. Analogue 88-85 affected the viscosity behavior the greatest and Analogue 88-82 the least. The other three analogues (88-33, 88-84, 88-92) demonstrated relatively similar VIs but slightly different viscosity behaviors, particularly at lower temperatures. It is notable, at first glance, that increasing VI does not correspond to increasing apparent molecular weights ($\bar{M}_{w,app}$). In particular, 88-85 has a VI of 247 and $\bar{M}_{w,app}$ of 465 kDa whereas 88-84 VI is slightly lower at 233 albeit the $\bar{M}_{w,app}$ is greater at 534 kDa. The non-uniformity, or molar dispersity (D_M), is greater for 88-85 (2.9) than 88-84 (2.3). The lower VI for 88-84 and 88-82 also suggests that a semi-crystalline inner core has no beneficial influence on

Table 2. Viscosity Performance of a 5% w/w [Additive]/[Yubase 4] Blend

	88-33	88-85	88-82	88-84	88-92	4Yubase	Bench2
cP @ 10 °C	170.4	188.4	88.8	187.2	166.6	55.74	
cP @ 25 °C	90.8	100	45.8	102	85.9	28.7	
cP @ 40 °C	52.98	58.98	26.34	59.8	49.35	15.92	
cP @ 60 °C	29.46	32.4	14.48	32.6	27.03	8.67	
cP @ 100 °C	12	13.58	6.06	13.02	11.15	3.54	
Density (g/cm ³)	0.833	0.832	0.835	0.831	0.832	0.825	
cSt @ 40 °C	63.60	70.89	31.54	71.96	59.31	19.30	
cSt @ 100 °C	14.41	16.32	7.26	15.67	13.40	4.29	7.69
VI	238.49	247.15	206.42	232.55	234.97	131.79	~200
SSI*	35.1	33.0	15.0	23.5	33.2	n/m	30.7

*Shear stability test CEC L-45, 20 h, 100°C. DV of blended oils (additive/oil) was measured by a Brookfield spindle viscometer and recorded in centipoise (cP) at 10°C, 25°C, 40°C, 60°C, and 100°C. KV was calculated for 40°C and 100°C by dividing DV by their respective additive/oil densities. VIs were determined via an online calculator from the aforementioned KV values. The SSI values were evaluated via CEC L-45-99 test, at Southwest Research Institute.

viscosity performance. The KVs, VIs and shear stability indices (SSIs) are reported in Table 2.

Two of the analogues have exceptional SSIs, being 100% or 50% lower than reference state-of-the-art VIIs. This behavior is not connected with their respective molecular weight, as these analogues do not possess the lowest molecular weight. Typically low molecular weight polymers tend to have high SSIs. The source of this positive yet unexpected result is not yet elucidated and it is still an active area of research.

Task 4

Lastly, base fluid viscosities were studied. Simulations of trimethyloleate predicted a 40°C viscosity of 38.7 cSt, which was very close to the experimentally measured value. However, simulations of the triazine analog 61828-39R significantly overpredicted viscosity. Analyses of the interatomic model (force field) indicated that the issue was related to the model of the atomic interactions at the molecule's center ring. We are in the process of performing density functional theory calculations with which we can tune the force field to enable more accurate viscosity predictions in MD.

Conclusions

- A short series of polyamines and polyesters as a multi-functional base oils were scaled-up. The KV, VI and pour point of six of the compounds which were fluidic at RT, were evaluated.
- The respective base oils were evaluated for friction and only the polyester has a desirable friction profile as a neat material.
- SANS, DLS, and MD simulations provide good tools for studying molecular conformations of polymers, but do not correlate well with the respective VIs.
- Hyperbranched polymers can provide a significant improvement in shear stability, as high as nearly 100% versus state-of-the-art VIIs.

References

1. Priyanka Bhattacharya, Uma Shantini Ramasamy, Susan Krueger, Joshua W. Robinson, Barbara J. Tarasevich, Ashlie Martini, and Lelia Cosimbescu*; Trends in Thermoresponsive Behavior of Lipophilic Polymers; *Industrial & Engineering Chemistry Research*; DOI: 10.1021/acs.iecr.6b03812.

FY 2016 Publications/Presentations

1. Priyanka Bhattacharya, Uma Shantini Ramasamy, Susan Krueger, Joshua W. Robinson, Barbara J. Tarasevich, Ashlie Martini, and Lelia Cosimbescu*; Trends in Thermoresponsive Behavior of Lipophilic Polymers; *Industrial & Engineering Chemistry Research*; DOI: 10.1021/acs.iecr.6b03812..
2. High Efficiency Lubricant Oils and Additives Research Annual Report 2015 – PNNL -25081.
3. Viscosity Modifiers: A Fundamental Study; Lelia Cosimbescu (presenter); B. Tarasevich; P. Bhattacharya; J. Robinson; S. Krueger; U.S. Ramasamy; A. Martini; 71st STLE Annual Meeting & Exhibition on May 15, 2016, Las Vegas, NV, United States.

V.15 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, polarity, and ability to affect the viscosity and friction performance of a base oil
- Evaluate fuel efficiency performance of the engine utilizing fully formulated oil
- Demonstrate at least a 2% improvement in fuel economy standardized tests

Fiscal Year (FY) 2016 Objectives

- Achieve an acceptable GF-5 oil blend by evaluating viscosity performance of fully formulated oil containing the viscosity index improver developed
- Conduct two independent engine tests
- Quantify fuel efficiency performance of the engine utilizing fully formulated oil
- Demonstrate at least a 2% improvement in fuel economy standardized tests

FY 2016 Accomplishments

- Generated 11 gal of finished formulated oil
- Attained the 2013 technical target of a minimum of 2% fuel economy improvement (FEI) in a light-duty vehicle using PNNL viscosity index improver
- Demonstrated that the viscosity index improver (VII) can be formulated in a 0W-30 engine oil
- Conducted blend studies to optimize the concentration of the VII in the finished formulation
- Worked with collaborators to conduct the Federal Test Procedure which is equivalent to a Sequence VID fuel economy test

**Lelia Cosimbescu (Primary Contact),
Joshua Robinson, J. Timothy Bays,
Brian West***

Pacific Northwest National Laboratory (PNNL)
PO Box 999
Richland, WA 99352
Phone: (509) 375-6478
Email: lelia.cosimbescu@pnnl.gov

DOE Technology Development Manager:
Michael Weismiller

NETL Project Manager:
Carl Maronde

Information Release #PNNL-26105

Subcontractors:

*Oak Ridge National Laboratory,
Oak Ridge, TN

- Independently, a Sequence VIE fuel economy test was carried out and both tests confirmed a 2% FEI
- Three papers capturing our research were published

Future Directions

The project reached an end at the end of FY 2016 and there are no issues remaining. Follow-on work is planned under the lab call funded in FY 2017. ■

Introduction

The project seeks to increase fuel efficiency by employing novel molecular designs of VIIs, 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 has designed hyperbranched, moderately branched, and multi-branched polymers useful over practical temperature ranges, while ensuring that the resulting additives are compatible with existing lubricant packages for easy introduction to the legacy vehicle fleet. The present report illustrates results obtained using one of the materials developed.

Approach

A blend study was conducted to determine the required polymer concentration in the final formulation to achieve a 0W-30 or a 0W-20 finished oil, which included the determination of cold crank viscosity, ASTM D5293, using a cold crank simulator (CCS) and high temperature high shear (HTHS), ASTM D5481. It should be noted that this blend study was by no means part of any optimization process. The formulation was not optimized, instead a generic formulation suggested by our industrial partners and base oil providers was utilized; a dispersant inhibitor package containing all lubricant additives, except for the viscosity modifier, was a fixed 10.1% (w/w), the VII is a variable (to be determined), and the rest, up to 100%, was the base oil (Yubase 4). The tests were performed according to industry standards, by industrial partners.

Results

A blend study (Table 1) was conducted to determine the required polymer concentration in the final formulation as well as the viscosity grade.

A 0W oil is required to have a maximum low temperature cranking viscosity of 6,200 cp (7,389 cSt) and our oil

meets this criteria successfully being well below that limit. However, the HTHS value was difficult to achieve as the 2% concentration yielded a formulation with too high of a kinematic viscosity at 100°C, but too small of a value for the HTHS to be rated as 0W-30. In industry it is possible to “tweak” the formulation to bring all values to fall under a particular viscosity grade, but that may take years of experience and time. We compromised in choosing a polymer concentration that met the 0W-30 viscosity grade values, with the exception of HTHS, which fell under the 0W-20 viscosity grade at 2.6 cP. As such, the final formulation contained 1.538% PNNL polymer (Analogue 33) and had the kinematic viscosity characteristics as shown in Table 2.

Eleven gallons of this formulated lubricant (1.538% polymer, 10.1% dispersant inhibitor package, up to 100% Yubase 4) were generated to accommodate two engine tests to evaluate fuel economy improvements provided by the lubricant. Both tests were referenced to an ASTM base lubricant (BL) for comparison, which is a 20W-30 oil.

The first engine test was run by Brian West at Oak Ridge National Laboratory who has developed a vehicle-based test protocol that mimics the ASTM D7589

Table 1. Blend Study of Various Polymer Concentrations in a Full Package Formulation

Conc. (wt%)	40°C (cSt)	100°C (cSt)	VI	HTHS (150°C; cP)	CCS (-35°C; cP)
1.0 (117E)	44.1	9.6	210.4	2.29	4962
1.5 (117D)	55.5	12	219.8	2.54	5184
2.0 (117A)	70.1	15.4	233.8	2.8	5962
4.0 (117B)	142.1	31.4	263.4	N/M*	N/M
6.0 (117C)	247	55.1	284.6	N/M	N/M

VI - viscosity index

The oil density of the blends was uniform at 0.84 g/mL. * N/M indicates not measured, due to an out of range 100°C viscosity.

Table 2. Viscosity Parameters of Scale-Up Formulation Containing PNNL VII

Conc. (wt%)	40°C (cSt)	100°C (cSt)	VI	HTHS (150°C; cP)	CCS (-35°C; cP)
1.538	56.56	12.46	225	~2.6 ^a	>5184 ^b

^a The value at 1.5% was 2.54 cP, so the value is expected to be at least 2.6 cP with the slightly increased polymer concentration. The final value was not measured. ^b The CCS value must be slightly higher than 5,184 cP, although it was not measured.

(Sequence VID). Fuel economy was measured for the three-phase Federal Test Procedure (also known as the city test), the Highway Fuel Economy Test, and a custom steady-state fuel economy test for steady cruise speeds from 40 mph to 80 mph in 5 mph increments. Comparing the PNNL test lubricant to the average of the BL runs, the following observations can be made about fuel economy improvement of the 2013 Chevrolet Silverado pickup truck equipped with the 4.8-L, pushrod V8 engine:

- City fuel economy improves 2.3% (composite three-bag result)
 - 4% on the cold Bag 1
 - Less than 2% on Bags 2 and 3
- Highway Fuel Economy Test fuel economy improvement of 1.7%
- Custom steady-state fuel economy test improvement ranges from 1% to 2%, with higher improvement measured at lower speeds

The second engine test was a Sequence VIE test, under development at Southwest Research Institute®, (in lieu of a Sequence VID) which evaluates a lubricant’s fuel economy compared to a baseline 20W-30 mineral oil. The same industrial baseline lubricant was used for both independent tests at Southwest Research Institute and Oak Ridge National Laboratory. A 2012 model year General Motors V6, 3.6-L port fuel injected gasoline engine is used in the VIE procedure. This test involves a set of stages as well as aging the candidate oil as follows: the baseline oil is run first (BL-4, BL Before) followed by a flying flush of the candidate oil. That oil then runs for 16 h of aging conditions and then the same stages as the baseline oil to compare fuel consumed. This is used to calculate FEI 1. The oil is then aged another 109 h and the candidate stages run again to calculate FEI 2. A flush oil removes the candidate oil, and BL-4 is then flushed back into the engine to obtain a BL after portion of the test. A comparison is made using 80% weighting for BL Before and 20% for BL After to provide FEI 1 results, and 90% BL After and 10% BLB 2 for FEI 2. The results of the test are summarized in Table 3.

Table 3. Sequence VIE Test Results

FEI 1 80/20 Engine Hours Adjusted	1.11%
FEI 2 10/90 Engine Hours Adjusted	0.9%
FEI Sum	2.01%

Conclusions

Given that the Sequence VIE is a pass/fail test against a GF-5 platform, which requires a minimum of a 2.0% FEI sum, we can conclude that this lubricant has acceptable performance for industry adoption.

The Sequence VID mimic and Sequence VIE tests note a FEI that meets the project requirements. Furthermore, work to develop an optimized formulation is expected to significantly improve the FEI performance beyond that measured in this study.

FY 2016 Publications/Presentations

1. Lelia Cosimbescu*, Joshua W. Robinson, Yan Zhou, Jun Qu; Dual functional star polymers for lubricants; *RSC Adv.*, 2016, **6**, 86259–86268.
2. Joshua W. Robinson, Yan Zhou, Jun Qu, J. Timothy Bays, Lelia Cosimbescu*; Highly branched polyethylenes as lubricant viscosity and friction modifiers; *Reactive and Functional Polymers*, 2016, **109**, 52–55.
3. Robinson, J.W., Zhou, Y., Qu, J., Erck, R. and Cosimbescu, L. (2016), Effects of star-shaped poly(alkyl methacrylate) arm uniformity on lubricant properties. *J. Appl. Polym. Sci.*, 133, 43611.
4. Robinson, J.W.; Zhou, Y.; Bhattacharya, P.; Erck, R.; Qu, J.; Bays, J.T.; Cosimbescu, L. “Probing the molecular design of hyper-branched aryl polyesters towards lubricant applications.” *Sci. Rep.* 2016, **6**, 18624.
5. Final Report 2016: “Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils,” PNNL-25806.
6. Annual report: Cosimbescu L, J.W. Robinson, and J.T. Bays. 2015. Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils. PNNL-25088.
7. Hyperbranched Alkanes for Lubes; June 11, 2016, AMR, Washington, D.C.
8. Robinson J.W., Zhou Y., Erck R., Qu J., Cosimbescu L., “Perfecting the Lubricant Wheel through Macromolecular Design,” 71st STLE Annual Meeting & Exhibition on May 15, 2016, Las Vegas, NV, United States.

Special Recognitions and Awards/ Patents Issued

1. As a result of this project, the viscosity index improver technology was selected for the Lab Corps Program (Lab Cohort 4).

VI. Advanced Fuels & Engines

This section will detail ongoing projects to advance economic and energy security through early-stage research on advanced engines and emerging domestic fuels.

VI.1 Gasoline Engine and Fuels Offering Reduced Fuel Consumption and Emissions (GEFORCE)

Overall Objectives

ORNL is establishing key engine technologies and fuel characteristics that enable very high fuel efficiency with very low emissions in future vehicles.

Fiscal Year (FY) 2016 Objectives

- Complete production of the fuels in the experimental fuel matrix
- Complete installation and baseline studies of 2.0-L General Motors (GM) LTG engine
- Receive and commission advanced research engine to support fuel studies

FY 2016 Accomplishments

- Completed production of all fuels for the project
- Commissioned and conducted baseline data collection on a 2.0-L GM LTG engine
- Conducted vehicle modeling of a mid-size sedan on multiple drive cycles using data from the baseline LTG engine

Future Directions

ORNL will identify path forward for calibration of advanced research engine to enable completion of project objectives. ■

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.

Scott Sluder (Primary Contact), Martin Wissink, Mike Viola (General Motors and Coordinating Research Council AVFL-26)

Oak Ridge National Laboratory (ORNL)

2360 Cherahala Blvd.

Knoxville, TN 37932

Phone: (865) 946-1235

Email: sluders@ornl.gov

DOE Technology Development Manager:

Kevin Stork

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 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 time frame. 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 Coordinating Research Council 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

Production of the fuels for this project was completed this year. The matrix includes 16 fuel formulations that span ethanol concentrations from 0% to 30% by volume, with Research Octane Number levels from 92 to 102 and three levels of final boiling point. Multiple drums of each formulation were produced to support engine operations. The fuels are stored at a logistics facility in the Detroit area for shipment to ORNL as needed to support the project.

A GM 2.0-L four-cylinder LTG engine and controller were provided by GM for use at ORNL in establishing baseline fuel consumption and emissions results. Figure 1 shows a photograph of the engine installed in an engine research laboratory at ORNL. The emissions results will primarily provide guidelines for use in the calibration of the advanced engine for the research fuels. The fuel consumption data were used to establish a baseline vehicle fuel economy value using emissions certification gasoline for the target vehicle by using a vehicle model in Autonomie. Figure 2 shows a map of the torque and speed conditions at which fuel consumption and emissions data were collected. Engine speeds of 1,000–2,500 rpm

were targeted since the majority of certification driving schedule operation occurs in this speed range. Data were also collected at 5,000 rpm to provide a means of interpolating the results to obtain fuel consumption values at intermediate speeds. This approach has also been used in other related studies that are examining opportunities for increased octane ratings to produce improved engine and vehicle fuel efficiency. For this baseline condition, the engine control unit controlled spark timing and knock avoidance according to its production calibration.

The engine data gathered using the LTG engine were used to support a vehicle model in Autonomie. The vehicle model targeted a current mid-size sedan with industry-average aerodynamic and mass characteristics. The baseline vehicle was modeled using target dynamometer coefficients and test weight

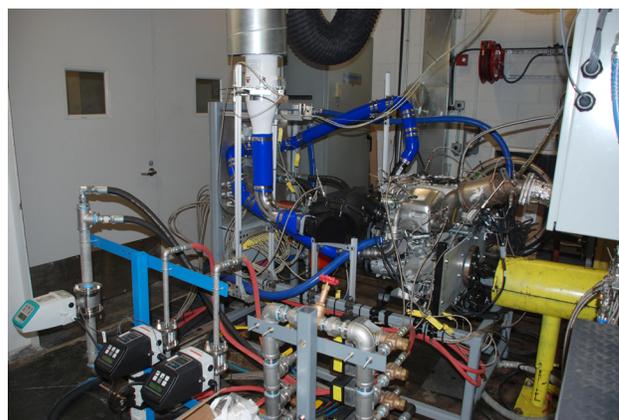


Figure 1. Photograph of installation of GM 2.0-L LTG engine for baseline data collection

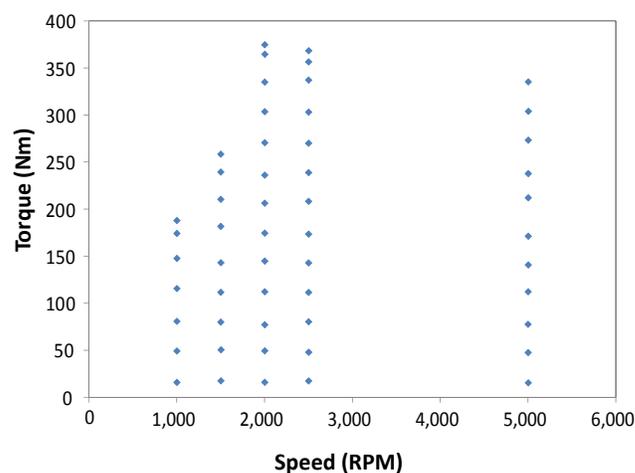


Figure 2. Map of the torque and speed conditions where baseline data from the LTG engine were collected

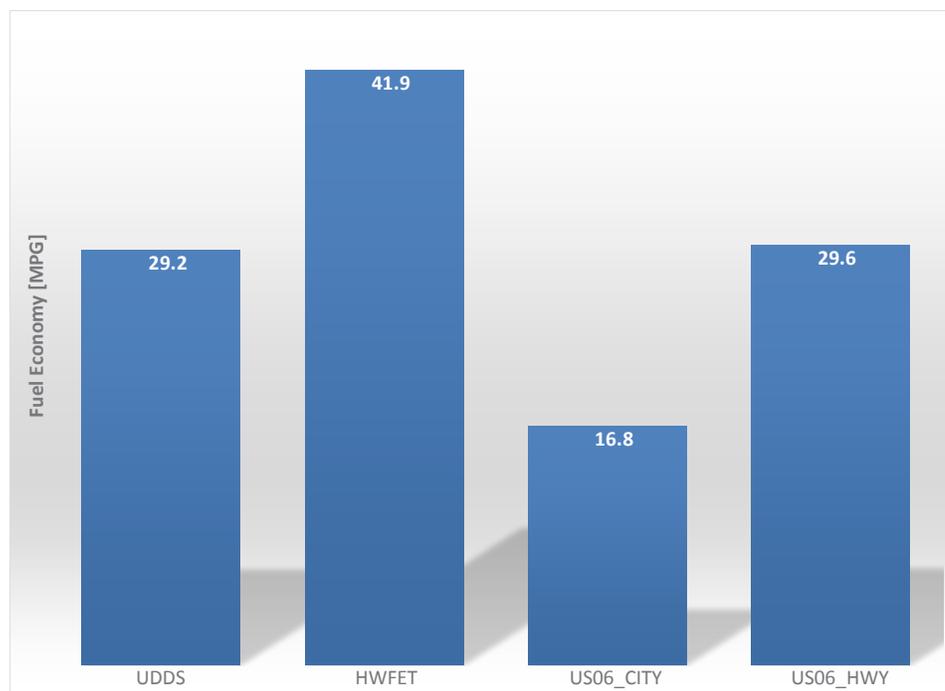


Figure 3. Baseline vehicle model fuel economy results

as follows: $A = 34.7297$ lbf, $B = 0.2821$ lbf/mph, $C = 0.0174$ lbf/mph², and engineering test weight = 4,000 lb. Transmission and final drive ratios were taken from a vehicle equipped with the LTG engine. The vehicle model was exercised using the speed-time profiles for the Urban Dynamometer Driving Schedule (UDDS), the Highway Fuel Economy Test (HWFET), and the city and highway portions of the US06 cycle. Figure 3 shows the fuel economy results from this baseline case.

In July of 2016, GM reached an impasse in their efforts to identify internal resources to complete calibration of the advanced research engine. The engine assembly was completed, however, substantial work was needed to integrate the control code necessary for the two-stage turbocharger and the exhaust gas recirculation system on the modified research engine. Several options are being explored for completing the calibration of the engine, however, this situation prevented delivery of an operational engine to ORNL this fiscal year. Efforts are ongoing to resolve this issue.

Conclusions

- Production of the extensive matrix of fuels to support this research project was completed this year.
- Installation and operation of a GM 2.0-L LTG engine was accomplished. Data were collected to support baseline vehicle modeling.
- Baseline vehicle modeling was completed using the data gathered from the LTG engine.
- Delivery of the advanced engine to ORNL has been delayed as a result of resource issues at GM. Solutions for this issue are being pursued.

VI.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) 2016 Objectives

- Complete one- and two-dimensional nuclear magnetic resonance (NMR) spectroscopy, and gas chromatographic analyses to correlate a 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

FY 2016 Accomplishments

- Applied solid state ^{13}C NMR to probe shale oil samples, fresh and spent, examining the organic material that was turned into fuel components, as well as the residual organic material remaining in the shale
- Continued collaboration with CanmetENERGY and further refined structure–property relationships for diesel fuel lubricity using NMR and gas chromatography–field ionization mass spectrometry data

Future Directions

- This project will be closed out and the results for fuels derived from shale oil reported in a publication.
- Structure–property relationships explored under this project will be continued under Co-Optima. ■

Introduction

The objective of this project was 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

Tim Bays (Primary Contact), John Linehan, and Sarah Burton

Pacific Northwest National Laboratory (PNNL)
PO Box 999
Richland, WA 99352
Phone: (509) 375-6900
Email: tim.bays@pnnl.gov

DOE Technology Development Manager:
Kevin Stork

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 worked 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 has worked to 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. These and other correlations were developed and will be expanded under the DOE Co-Optima project. In finishing out this project, we are examining the structures that are present within the shale itself, expecting this information to be combined with previous data and published.

Approach

PNNL examined a variety of fuel 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. 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 heteronuclear single quantum coherence, and two-dimensional gas chromatography. The results of these analyses are then combined through regression-based modeling methods to tie fuel performance properties, such as lubricity, to specific molecular substructures. Our goal is to establish chemical structure–property correlations to ensure fuel compatibility with existing engines, and expand molecular-based blending models to quantify contributions of fuels from alternate feedstocks entering into the market. 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 previous 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. Early results related to the shale oil-derived fuels were published and presented previously [1]. A more detailed set of results reflecting further study of the shale oil-derived fuel samples is expected to be published in the near future. The knowledge gained in this project is expected to be applied in the Co-Optima project.

In finishing our shale oil-derived fuel work, solid state, magic angle spinning ^{13}C NMR analyses were performed on samples from Red Leaf Resources, Incorporated, of the kerogen-containing shale from which our shale oil fuels samples were derived, as well as samples of shale following the extraction processes used by Red Leaf. The kerogen-containing shale sample is referred to as “as received,” and the shale sample following extraction of the kerogenic material is referred to as “spent.” The resulting ^{13}C NMR spectra of an “as received” shale-oil sample and a “spent” shale-oil sample are compared in the Figure 1. For each of the solid state carbon spectra shown, there are two distinct resonances, one in the aliphatic region and one in the aromatic region. The area under each resonance can be compared allowing a quantitative comparison of each carbon type, as well as quantitative comparison between the spectra. Notice that the area of the aliphatic (paraffin-like, resonances centered

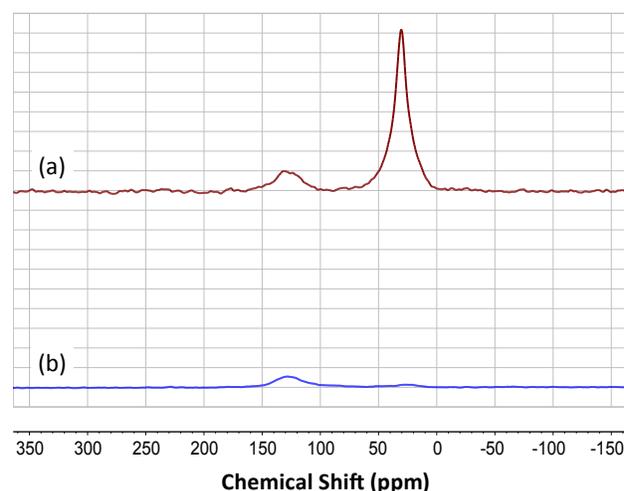


Figure 1. Comparison of the solid state ^{13}C NMR spectra for kerogenic shale from Red Leaf Resources, Incorporated (a) and spent shale following extraction of carbon and conversion to crude oil. Both spectra show two major resonances, one at about 125 ppm and a second at about 25 ppm, which represent aromatic carbons and aliphatic carbons, respectively. Differences between (a) and (b) are clear, showing the depletion of the aliphatic carbons by approximately 95%, with approximately a 50% reduction in the aromatic carbons. The spectra are compared using an absolute scale.

at 25 ppm) components is reduced by over 95% as a result of the extraction, while the aromatic components (resonances centered at 125 ppm) are only halved by the extraction process. The ratio of aromatic to aliphatic carbons changes from nearly 1:5 to about 5:1. Further analysis of these spectra will aid in better assigning the underlying structure of these resonances to more specific carbon types. The direct NMR evidence of carbon types within the kerogenic materials demonstrates that the NMR techniques can identify extraction components and may lead to more efficient extraction technologies.

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.
- Solid state NMR analyses can yield important information about the natural resources and the processes used to extract usable fuels from those resources.

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 ^{13}C 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 ^{13}C NMR characterization of oil shale crude at various process stages of distillate fuel production*, American Chemical Society: 2014; pp ENFL-347.

VI.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 and 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) 2016 Objectives

- Deliver a steady-state calibration capable of meeting 50% petroleum reduction
- Deliver a transient calibration capable of meeting 50% petroleum reduction
- Perform engine and aftertreatment testing to support and validate petroleum reduction and emissions compliance targets
- Build a heavy-duty Class 8 dual-fuel vehicle
- Perform a vehicle demonstration of the Class 8 dual-fuel vehicle

FY 2016 Accomplishments

- Demonstrated 50% petroleum reduction over Ramped Modal Cycle Supplemental Emissions Test (RMCSET) cycle
- Demonstrated 50% petroleum reduction over hot Federal Test Procedure (FTP) cycle
- Built a heavy-duty Class 8 dual-fuel vehicle

Future Directions

- Demonstrate petroleum reduction with final emissions capable calibration
- Perform vehicle demonstration of the Class 8 dual-fuel vehicle ■

Lyle Kocher

Cummins Inc.
1900 McKinley Avenue
Columbus, IN 47201-6414
Phone: (812) 377-2507
Email: lyle.e.kocher@cummins.com

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager:
Walter Parker

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 (E85 [85% ethanol, 15% gasoline blend]), 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 port fuel injection 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 the dual-fuel engine into a Class 8 vehicle. A Peterbilt 587 vehicle was selected as the target vehicle. A major design feature was the addition of the E85 fuel handling system. The passenger side fuel tank was converted for use with E85 and a fuel system module was added along the frame rail of the vehicle near the fuel tank. The fuel module incorporated a pre-filter, fuel pump, pressure regulator, fuel filter, and instrumentation for temperature, pressure, and flow. A second design feature was the addition of the National Instruments CompactRIO controls system. The unit was mounted in the sleeper portion of the cabin with the harnessing run into the engine compartment. The vehicle build was completed in December 2016.

Combustion Computational Fluid Dynamics Analysis

The combustion development of a new dual-fuel premixed compression ignition engine has been conducted using three-dimensional computational fluid dynamics 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 2016, extensive computational fluid dynamics work focused on understanding the sensitivity and impacts of these elements to provide a robust combustion system design. Two potential pitfalls for a combustion simulation is the accuracy of the flow field and the accuracy of the chemical kinetic reaction mechanism. Throughout the course of the program, a number of engine experimental conditions were not able to be modeled with the desired level of accuracy. The team implemented a full cycle simulation to capture the effect of the flow field on the combustion event. A comparison of the flow field from various combustion simulation types is shown in Figure 1. The flow field on the left is from a sector defined model as typically used in diesel combustion simulation. The middle flow field is from a 360° model initialized with solid body rotation. The right flow field is from a full cycle simulation that models the intake port flow and valve movement. While the full cycle simulation improved the overall accuracy of the model, the model prediction was still not as desired. The team also examined several available reaction mechanisms available in literature. None of the available mechanisms were

better at prediction than the original mechanism hence the team tuned the existing mechanism to better represent the engine experimental observations. Future work in this area should include efforts to improve the detailed chemical reaction mechanism for dual fuel combustion.

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 in-cylinder pressure sensor processing system, engine control unit, port fuel injection control module, and National Instruments CompactRIO controls system. Each component was developed and bench-tested in the laboratory before being deployed at the test cell. The National Instruments CompactRIO system is the central component of the controls system. It implements advanced controls technologies to control combustion phasing, as shown in Figure 2, by interfacing with the engine control unit. 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 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. The model was used extensively to test the robustness of the controls system and model off-nominal conditions.

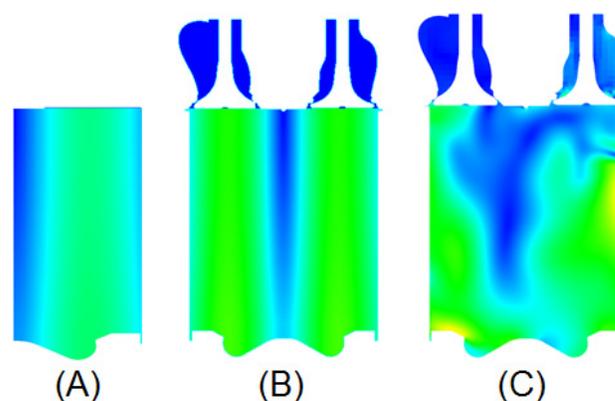


Figure 1. Flow fields, (A) sector defined, (B) 360°, and (C) full cycle simulation

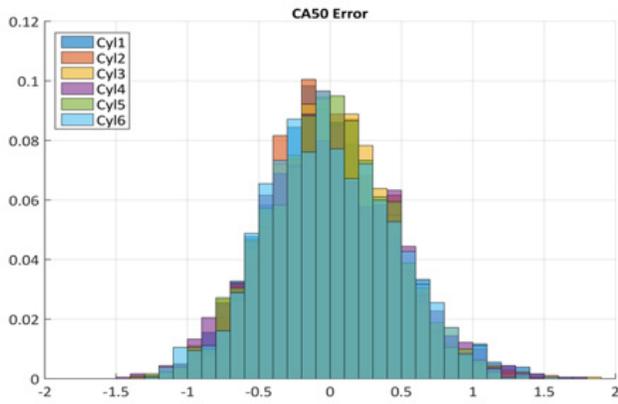


Figure 2. Crank angle at 50% fuel energy release (CA50) error histogram

Engine Testing

The first half of 2016 focused on delivering a steady-state calibration capable of meeting the desired emissions and petroleum reduction performance targets. The calibration was optimized on the combustion system hardware selected through the analysis-led design process. The details of the combustion system development were shown at the Annual Merit Review [1]. In the second half of 2016, the focus shifted to delivering a transient capable calibration with a focus on demonstrating 50% petroleum reduction over the RMCSET and FTP test cycles. Figure 3 shows the cumulative petroleum reduction over a hot FTP cycle. The current calibration is meeting the petroleum reduction target. Optimization work is in progress to calibrate the aftertreatment controls to meet the cycle emissions targets and maintain the petroleum reduction while operating the engine on E85 and diesel fuel.

Conclusions

The Cummins EDPCI E85–diesel dual-fuel engine program has successfully completed the first 18 months of the 24-month program. The following conclusions have come from the program thus far:

- A dual-fuel engine can be designed and developed to demonstrate a 50% petroleum reduction over the RMCSET cycle.

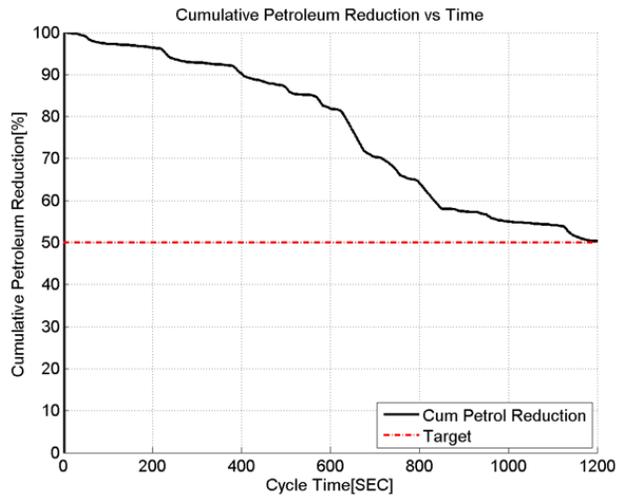


Figure 3. Cumulative petroleum reduction over hot FTP cycle

- A dual-fuel engine can be designed and developed to demonstrate a 50% petroleum reduction over the hot FTP cycle (and expected to be achieved over full FTP).
- A dual-fuel engine can be designed and developed to demonstrate comparable engine performance and full load capability compared to a diesel engine.
- 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. Lyle Kocher, *Cummins EDPCI Project: E85/Diesel Premixed Compression Ignition*, Cummins, 2016 DOE Vehicle Technologies Program Annual Merit Review, Washington, D.C., June 9, 2016.

VI.4 Utilizing Alternative Fuel Ignition Properties to Improve SI and CI Engine Efficiency

Overall Objectives

UM will demonstrate 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 (SI) engines and greater than 50% for compression-ignited (CI) engines.

Fiscal Year (FY) 2016 Objectives

- Develop spray and spark timing strategies for different fuel compositions and blends (include effects of exhaust gas recirculation [EGR]) that quantify sensitivity to extending knock limits and enable higher engine efficiencies using a production multi-cylinder gasoline turbocharged direct injection (GTDI) engine, a single-cylinder GTDI engine facility using production hardware, and an experimental single-cylinder engine facility equipped with two independent fueling systems
- Assess the impact of multiple fuel injection pulses on knock mitigation and engine emissions for different fuel blends with production hardware
- Configure system level models using GT-POWER for fuel evaporation and compare with single-cylinder efficiency results
- Use detailed kinetics simulations of knock for ethanol and ethanol blends and compare with experimental knock limits

FY 2016 Accomplishments

- A GT-POWER model of fuel evaporation was developed with good agreement with experimental data.
- A detailed kinetic fuel model was used to characterize knock limited load data from the literature.
- Major improvement in the range of maximum brake torque (MBT) operation of the production single-cylinder engine was demonstrated by blending gasoline with ethanol, with a maximum gross indicated thermal efficiency (GTE) of 38.4%.
- A state-of-the-art, production, multi-cylinder GTDI engine was installed and instrumented for fuel effects studies and a design of experiments was developed and applied to fuel injection and fuel blend studies. The results of the design of experiments were analyzed and

Margaret S. Wooldridge (Primary Contact), André Boehman, George Lavoie

University of Michigan (UM)
Department of Mechanical Engineering
2350 Hayward St.
Ann Arbor, MI 48109
Phone: (734) 936-0349
Email: mswool@umich.edu

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager:
Carl Maronde

Partner:
Bosch LLC

interpreted to create fuel injection strategies for optimal thermal efficiency.

- Approximately four percentage point increase in brake thermal efficiency (BTE) was achieved with E85 (85% ethanol, 15% gasoline blend) compared with gasoline using the multi-cylinder engine facility.
- E85 yielded significantly lower exhaust temperatures for the same load conditions compared with gasoline which reduced the losses due to fuel enrichment for component protection.
- A port fuel injection (PFI) cylinder head was modified for combined direct injection (DI)+PFI operation on a single-cylinder Hydra engine.
- A study of the effects of syngas (simulated fuel reformate) addition to gasoline for knock suppression was completed using the Hydra test engine.

Future Directions

- Complete DI fuel injection controls development and perform combined DI+PFI stratified and multiple-injection DI stratified fueling studies to assess impacts of fueling strategy on knock suppression in the Hydra.

- Assess tradeoffs between particulate mass/particulate number emissions and knock suppression for fueling strategies in the Hydra and the multi-cylinder test engines.
- Evaluate the in-cylinder soot formation in the multi-cylinder engine using in-cylinder imaging to identify the sources of soot and the effects of ethanol in soot suppression.
- Future engine and fuel modeling work will focus on integrating the models developed so far, calibrating with recent data and projecting possible engine benefits to vehicle fuel economy improvements. ■

Introduction

Downsized boosted SI engines offer considerable thermal efficiency benefits compared with 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 with 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 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 EGR. The objective of this work is to develop fuel injection and spark strategies which leverage the thermophysical properties of ethanol and other fuel supplements and EGR to maximize engine efficiencies.

Approach

A combination of experimental and modeling methods is used in the current project to identify strategies to achieve 45% thermal efficiency. Single- and multi-cylinder engine facilities are used to quantify the effects of fuel blends and fuel strategies, and modeling efforts are used to interpret and extrapolate the experimentally observed trends. Two single-cylinder engine platforms were used to study fuel blends using production engine hardware and

using experimental hardware. The experimental engine hardware (based on a Hydra engine) was used to study the effects of EGR to mitigate knock and comparison with syngas (H_2 and CO) addition to offset stability issues that occur with high dilution. The production single-cylinder engine hardware (a Ford Fox engine where two of the three cylinders were deactivated) was used to study the effects of varying levels of ethanol in ethanol-gasoline blends at a range of intake air pressures. The lessons learned from the fuel composition and fueling strategies were applied to multi-cylinder engine studies. In-kind support by Bosch was directed toward the single-cylinder and multi-cylinder engine studies.

Results

Simulations of Engine Efficiency Enhancement and Limitations

Figure 1 shows the results of the investigation of evaporation effects and how they relate to efficiency gains with ethanol and ethanol blends. The data are experimental results from the Fox single-cylinder GTDI engine at 1,000 rpm over a range of intake pressures from 100 kPa to 150 kPa. Crank angle for 50% burn (CA50) for all points was $\sim 10^\circ$ after top dead center (dATDC). The ethanol blends were able to operate without knock for all intake pressures while the gasoline point shown is for $P_{in} = 100$ kPa, which was the only knock-free condition for gasoline. For higher P_{in} , spark had to be retarded and these results are not shown in Figure 1. The curves indicate the GT-POWER simulations which employed a DI injector with the option to take the heat of vaporization from either the walls (with no change in intake temperature) or the intake charge (with significant cooling). Start of injection was -240 dATDC which corresponded to the engine tests which were all conducted with open valve injection timing.

The two main effects of ethanol are seen in Figure 1. The first is simple heat of vaporization (HoV) accounting and is apparent for the case with all heat of vaporization coming from the walls. Since the incoming fuel energy is computed for the liquid fuel, and the heat released is from the vapor state there is a net benefit for the ethanol fuel [4]. For pure ethanol, this about 3.5% in efficiency gain on a relative basis. The other effect from ethanol arises from charge cooling and burned gas temperature reduction which will improve gas properties, as well as reduce the amount of dissociation. This is an additional 3.5% for pure ethanol with a total gain of 7%. Similar calculations were carried out with cylinder heat transfer set to zero and the results were almost identical, suggesting that any heat transfer changes are small and do not contribute significantly to the efficiency gain with

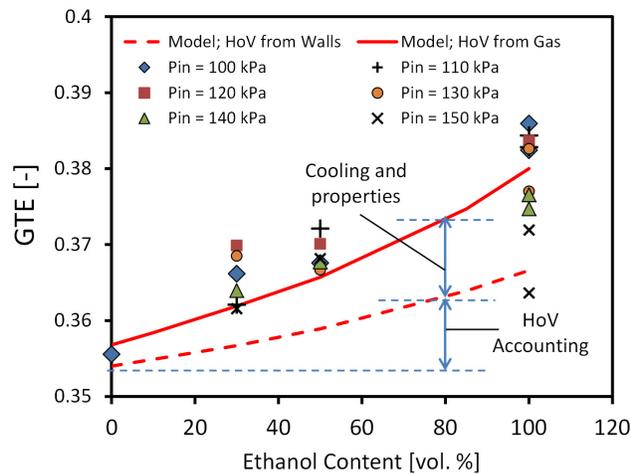


Figure 1. Comparison of GT-POWER simulation results (with all vaporization heat from the walls or with all vaporization heat from the gas) and experimental measurements of GTE as a function of ethanol content in the fuel. The experimental data are from the single-cylinder Fox GTDI engine for various intake pressures.

ethanol fuel. This disagrees with Jung et al., [4] and will be investigated further. Overall the model agrees well with the data. Almost all of the HoV appears to come from the gas. However, for the highest intake pressure (noted by the \times symbols in Figure 1) and at the highest ethanol levels (E100), there is a significant fall off in efficiency gain, perhaps due to a longer injection event and more impingement on the chamber walls. Future work will focus on later injection timings to explore wall wetting effects.

Figure 2 shows the results of modeling efforts to identify the impact of fuel ethanol content on knock limited load at 1,500 rpm. The experimental data are from a single-cylinder study by Stein et al. [5], where the authors used a variety of gasoline–ethanol fuel blends and injection strategies, as well as from experiments conducted in the UM Hydra single-cylinder engine. The Stein et al. [5] experiments used an 88 Research Octane Number gasoline and mixed 50% by volume with ethanol, with fuel injected upstream of the intake to eliminate the impact of differing heats of vaporization, while the intake manifold temperature was 52°C consistent with the Research Octane Number test conditions. The UM Hydra experiments used an 87 anti-knock index research gasoline at ~30°C intake manifold temperature. The experiments show a decreasing slope with increasing ethanol content, where the higher ethanol fuel blend enables a higher load for a given combustion phasing (CA50), and a higher load at the latest combustion phasing. The UM experimental data exhibits similar

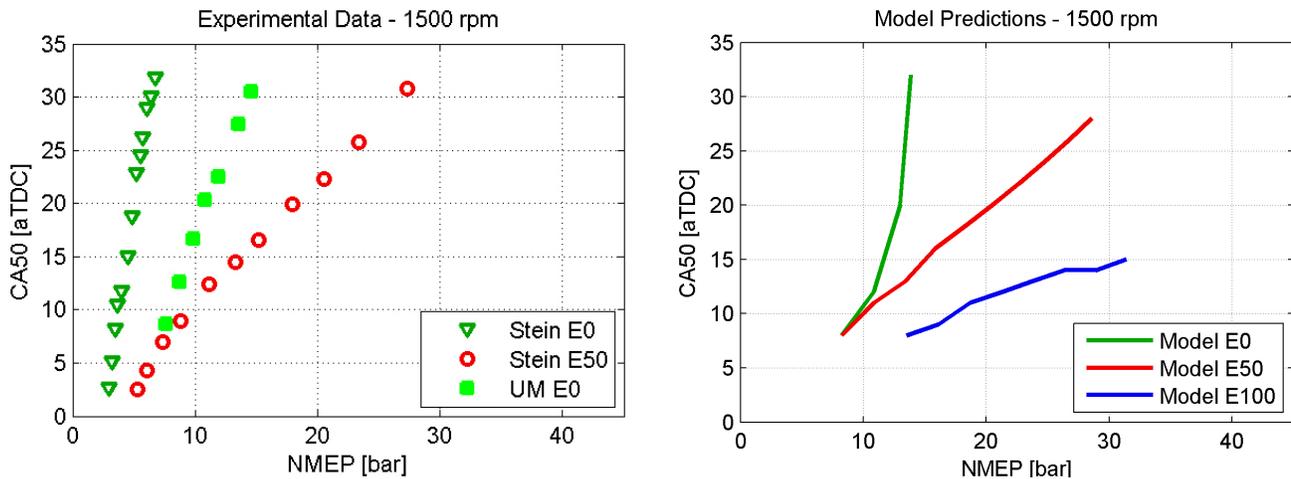
behavior to the Ford results for gasoline with no ethanol addition (E0), with a shift to higher loads consistent with the lower intake manifold temperature and higher octane rating both mitigating the tendency of the engine to knock.

A variable pressure reactor model was used to study the experimentally observed behavior. Pressure histories for this model were generated from a GT-POWER single-cylinder model, which was also used to estimate in-cylinder temperature and composition at intake valve closing. Intake manifold temperature was set to 52°C, while intake manifold pressure was changed from 0.4 bar to 2.6 bar (absolute) with exhaust manifold pressure constant at 1 bar. At each intake pressure CA50 was varied from 0 dATDC to 35 dATDC and combustion duration (CA10–90) was varied from 15 crank angle degrees to 30 crank angle degrees, using a Weibe function. The onset of knock was calculated using the gasoline surrogate mechanism of Mehl et al. [6,7], which includes an ethanol sub-mechanism and was developed to replicate 87 anti-knock index RD-387 research grade gasoline. Knock was defined to occur when the variable pressure reactor ignited (based on fuel mass burned). Overall the model agrees well with the experiments. The model predictions replicate the experimental trend of higher ethanol fuel blends having lower slopes and achieving higher loads at constant CA50. The E50 results agree well with the experiment in slope and magnitude. While the slope of the pure gasoline results agrees well with the experiments, the predicted net mean effective pressure values are all higher than the experiment. This is consistent with the model fuel surrogate having a lower reactivity, particularly in the negative temperature coefficient region, than the experimental fuel, as longer ignition delays would enable higher pressure operation prior to the onset of knock.

Future work will investigate the results sensitivity to the fuel surrogate reactivity by comparing several fuel surrogates and/or kinetic mechanisms. The model will also be exercised under conditions consistent with additional UM experiments using higher ethanol fuel blends as data become available.

Hydra Single-Cylinder Engine Studies of Syngas and EGR Dilution Effects on Extending Knock Limits

To explore the effects of the synthesis gas (syngas, mixtures of CO and H₂) supplementation on knocking under different dilution conditions, both stoichiometric and EGR–air diluted experimental conditions were considered. The intake pressure was varied from 0.4 bar to 1.6 bar at 0.1 bar intervals and spark timing was varied



aTDC – after top dead center; NMEP – net mean effective pressure; E50 – 50% ethanol, 50% gasoline blend

Figure 2. Comparison between experimental and modeled knock limits for gasoline-ethanol fuel blends. The left panel presents experimental data from Stein et al. [5] and the UM Hydra single-cylinder engine. The right panel presents the variable pressure reactor model results replicating the trend of decreasing slope and higher load limits with increased ethanol content.

at each intake pressure to find MBT and knock-limited conditions. The engine speed for all experiments was 1,500 rpm. The fuel energy was kept constant in all identical intake pressure conditions, and the syngas amount was controlled on an energy basis from 0% to 15% in 5% intervals.

Comparisons were made between supplementing the fuel with syngas and dilution with air and dilution with EGR. The effects on combustion phasing, thermal efficiency, combustion variability, knocking and engine emissions were quantified. Figure 3 shows the results for GTE. The data show at equivalent CA50 values the GTE is higher for air dilution in comparison with EGR dilution which is attributed to the higher ratio of specific heats for air versus EGR. However, at knock-limited boosted conditions, the GTE is higher with EGR dilution due to the extended knock limit enabled by EGR dilution. The thermal efficiency benefit of syngas addition is higher than the dilution benefit in the 0% to 15% syngas addition range, as shown in the knock-limited GTE results presented in Figure 4. The GTE consistently increased with increasing syngas levels, with a maximum improvement of 1.84% with syngas addition to EGR dilute conditions and a maximum improvement of 1.90% with syngas addition to air dilute conditions.

Single- and Multi-Cylinder Engine Studies of Ethanol Blend Effects on Increasing Engine Efficiency

Ethanol blends were studied using the Fox production single-cylinder engine and using the multi-cylinder GTDI production engine. Figure 5 presents the GTE from

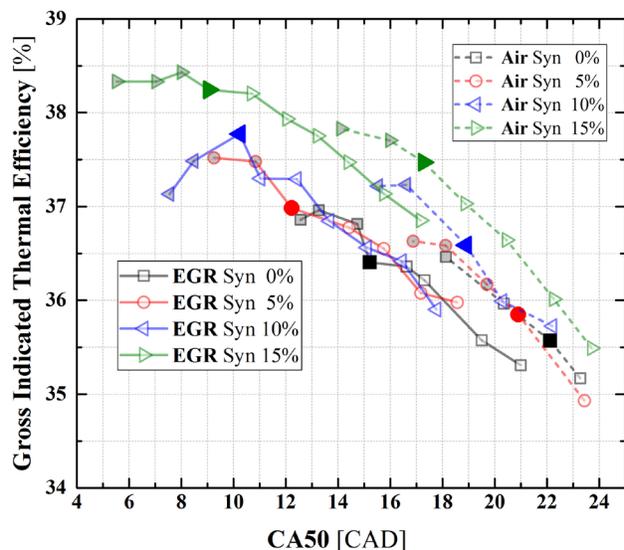


Figure 3. The effects of air and EGR dilution with varying levels of syngas addition to gasoline fuel. Emphasized symbols are MBT or knock-limited.

the Fox single-cylinder engine as a function of intake pressure and fuel blend. The engine was knock-limited at the operating conditions for E0, consequently GTE was systematically lower for E0 compared with the ethanol blends. The efficiency for E0 also decreased as intake pressure increased as the spark timing was retarded further from MBT. The gross efficiency of the E85 and E100 fuels were nearly identical, and the maximum GTE value was ~38% at intake pressures of 1.1 bar and 1.2 bar for E85 and E100.

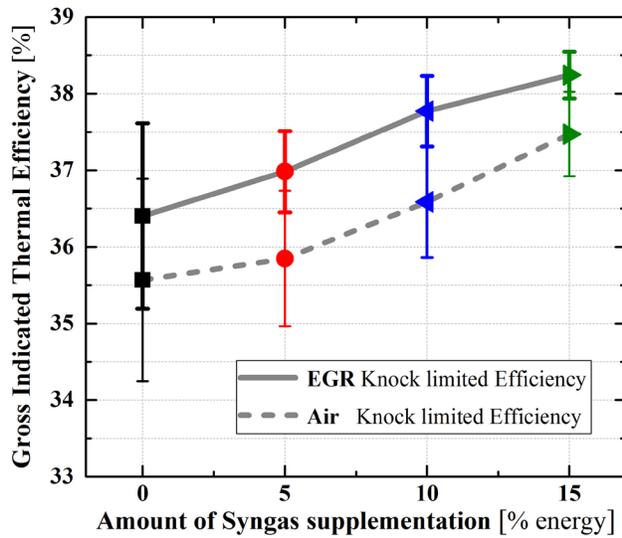
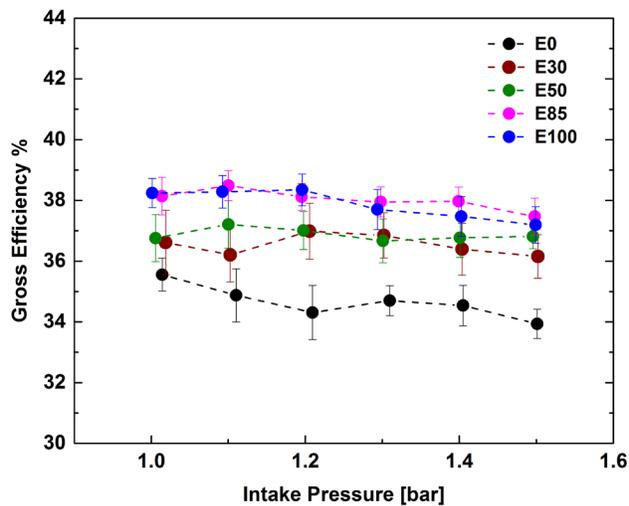


Figure 4. GTE as a function of syngas addition and type of charge dilution at knock-limited conditions



E30 - 30% ethanol, 70% gasoline blend

Figure 5. Effects of ethanol blends on GTE of GTDI single-cylinder engine for varying P_{in}

The BTE and brake mean effective pressure (BMEP) as a function of intake pressure for E85 and gasoline are presented in Figure 6. Higher efficiencies were achieved with E85 compared with gasoline over the whole load range of the engine. Approximately four percentage point increase in BTE was achieved with E85, reaching ~37% at the mid-load conditions. This was due to knock suppression of E85 and consequently the extended range of operation at MBT timing over a wider range of intake pressures with E85.

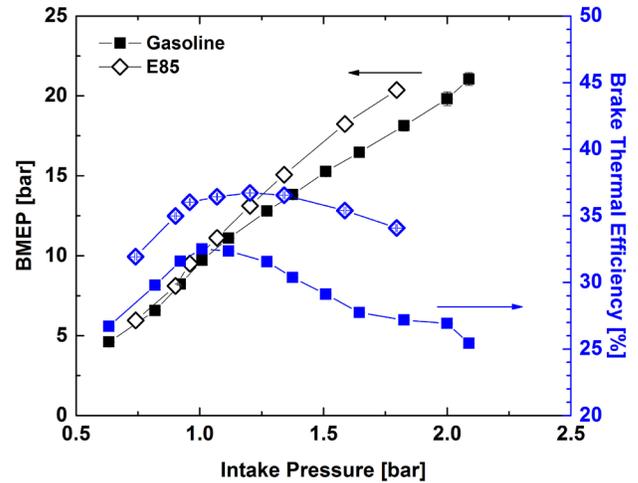


Figure 6. Comparison of BMEP and BTE for E0 and E85 at 1,750 rpm for varying P_{in}

Conclusions

- With the Hydra single-cylinder engine, experiments with syngas supplementation under EGR dilution and air dilution demonstrated that syngas addition efficiently mitigates engine knock under both boosted and diluted conditions. In addition, supplementing syngas is more beneficial under EGR dilution than under air dilution, from the perspective of not only knock mitigation but also thermal efficiency and emissions of oxides of nitrogen.
- With both the Fox single-cylinder and the GTDI multi-cylinder engine experiments ethanol yielded a major improvement in terms of expanding the range of MBT operation of the engine. However, there were diminishing returns to increasing the ethanol content beyond a threshold value in the blend if knock does not constrain engine operation. This is the same conclusion articulated by Stein et al. [8] in their comprehensive review of the effects of ethanol on engine performance.
- Modeling studies of gasoline–ethanol fuel blends have been used to gain insight into the impact of fuel effects on engine efficiency. GT-POWER simulations have shown half the gross thermal efficiency gain from ethanol over gasoline noted experimentally is due to the heat of vaporization accounting, while the other half is due to charge cooling and decreased burned gas temperatures. Variable pressure reactor simulations have qualitatively replicated the experimental increase in knock-limited load for increasing ethanol fuels.

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. Eng. Res.* 1-19.
3. Lewis, A.M., Ortiz-Soto, E., Lavoie, G., Assanis, D.N. (2015) "Scaling and dimensional methods to incorporate knock and flammability limits in models of high efficiency gasoline and ethanol engines," *Int. J. Eng. Res.*, 16, 181–196.
4. Jung, H.H., Shelby, M.H., Newman, C.E., and Stein, R.A. (2013) "Effect of ethanol on part load thermal efficiency and CO₂ emissions of SI engines," *SAE Int. J. Engines*, 6, 456–469.
5. Stein, R.A., Polovina, D., Roth, K., Foster, M., Lynskey, M., Whiting, T., Anderson, J.E., Shelby, M.H., Leone, T.G., VanderGriend, S. (2012) "Effect of heat of vaporization, chemical octane, and sensitivity on knock limit for ethanol - gasoline blends," *SAE Int. J. Fuels Lubr.*, 5, 823–843.
6. Mehl, M., Chen, J.Y., Pitz, W.J., Sarathy, S.M., and Westbrook, C.K. (2011) "An approach for formulating surrogates for gasoline with application toward a reduced surrogate mechanism for CFD engine modeling," *Energy Fuels*, 25, 5215–5223.
7. Mehl, M., Pitz, W.J., Westbrook, C.K., and Curran, H.J. (2011) "Kinetic modeling of gasoline surrogate components and mixtures under engine conditions," *Proc. Combust. Inst.*, 33, 193–200.
8. Stein, R.A., Anderson, J.E., and Wallington, T.J. (2013) "An Overview of the Effects of Ethanol-Gasoline Blends on SI Engine Performance, Fuel Efficiency, and Emissions," *SAE Int. J. Engines* 6, 470–487.

VI.5 Single-Fuel Reactivity Controlled Compression Ignition Combustion Enabled by Onboard Fuel Reformulation

Overall Objectives

- Reform gasoline, diesel, and natural gas to varying levels and characterize the constituent species of the reformate mixtures as well as the autoignition tendency of the reformate mixture in the form of an effective Primary Reference Fuel (PRF) number
- Evaluate the potential efficiency, emissions, operating range, and burn characteristics of reactivity controlled compression ignition using a parent fuel and its reformate mixture using computational fluid dynamics (CFD) simulations with detailed chemical kinetics as well as GT-SUITE models
- Experimentally test each parent fuel–reformate combination in reactivity controlled compression ignition (RCCI) and compare reformate RCCI to published RCCI data from the literature

Fiscal Year (FY) 2016 Objectives

- Construct a test facility to vaporize and reform gasoline, diesel, and natural gas to varying levels by accurately controlling the incoming and reactor temperatures as well as the flow rates of fuel and air through a catalyst
- Modify an existing Cooperative Fuel Research (CFR) engine to experimentally determine an effective PRF number of various reformate mixtures
- Reform gasoline, diesel, and natural gas to various levels and characterize the constituent species of the reformate mixtures using gas chromatography
- Create a PRF mapping by igniting blends of n-heptane and isooctane over a wide range of intake temperatures and compression ratios

FY 2016 Accomplishments

- The test facility was constructed to vaporize and reform gasoline, diesel, and natural gas to varying levels.
- The modifications to the existing CFR engine were made and the PRF mapping was created by igniting blends of n-heptane and isooctane over a wide range of intake temperatures and compression ratios.
- Gasoline, diesel, and natural gas were reformed to various levels and the constituent species of the

Benjamin Lawler (Primary Contact), Sotirios Mamalis, Dennis Assanis*

Stony Brook University

100 Nicolls Road

Stony Brook, NY 11794

Phone: (631) 632-8022

Email: benjamin.lawler@stonybrook.edu

* Dennis Assanis was formerly at Stony Brook University and currently the president of the University of Delaware

DOE Technology Development Manager:

Kevin Stork

NETL Project Manager:

Charles Alsup

Subcontractors:

- Dean Modroukas, Innoveering, LCC, Ronkonkoma, NY
- Marco Castaldi, City College of New York, New York, NY

reformate mixture were characterized using gas chromatography.

Future Directions

- In the following years, an effective PRF number of the reformate mixtures will be determined by autoigniting the reformate mixtures in homogeneous charge compression ignition (HCCI) combustion and comparing their results to the PRF mapping.
- CFD and GT-SUITE models will be created to evaluate the potential efficiency, emissions, operating range, and burn characteristics of the proposed concept using CFD simulations with detailed chemical kinetics as well as GT-SUITE models.
- Each parent fuel–reformate combination will then be experimentally tested in RCCI and comparisons between reformate RCCI and published RCCI data in the literature will be made. ■

Introduction

RCCI combustion has demonstrated efficiency and emissions improvements compared to both diesel and spark-ignited combustion modes [1–4]. Specifically, RCCI has demonstrated a 20% fuel economy increase compared to spark ignition [3], and a 5% efficiency improvement at certain engine speeds and loads over diesel while maintaining significantly lower engine-out soot and NO_x emissions [4]. However, RCCI is limited in its commercial viability due to the added cost and complexity of the two requisite fuel systems. To resolve this drawback and enable the commercialization of RCCI, the proposed innovation would use a single fuel with an onboard fuel reformer to create the necessary separation in fuel reactivity. In this proof-of-concept proposal, one branch of the fuel stream would be directed to the engine unaltered, while a second branch of the fuel stream would be processed with the onboard fuel reformer to produce reformat: a fuel mixture of H_2 , CO , and partially reacted hydrocarbon species whose properties are different from the initial parent fuel. The less reactive fuel will be port fuel injected and the higher reactivity fuel will be direct injected.

The approach is innovative because fuel reformer technology and RCCI combustion could potentially have a synergistic relationship. If successful, the proposed use of an onboard fuel reformer to create the necessary fuel reactivity separation from a single fuel would allow the future commercialization of RCCI and the realization of the previously reported benefits of RCCI.

Approach

The goal of this project is to determine the feasibility of RCCI combustion using a parent fuel and its reformat. Three potential parent fuels, diesel, gasoline, and natural gas, will be evaluated since these fuels are most relevant to vehicle applications. The approach to achieve this goal is first to reform the parent fuels to varying levels and characterize the species and autoignition properties of the reformat mixture. This first step will help in determining which parent fuels hold the most promise to enable reformat RCCI. Once the parent fuel and reformat combinations with the largest effective octane separation have been determined, CFD and system-level models will be used in conjunction with experimental testing to evaluate the potential efficiency, emissions, burn characteristics, and operating range of reformat RCCI. The model simulations and the experimental results of reformat RCCI will be compared to RCCI data in the literature to put the results in the greater context of the advanced combustion community and to help evaluate the feasibility and future promise of reformat RCCI.

Results

During the first year of this project, the test facility was constructed to reform the parent fuels to varying levels. Figure 1 is a photograph of this test facility showing the fuel cart that was designed to vaporize the liquid fuels and direct them through the catalyst and finally into gas chromatography instrumentation to measure the percentages of each species. Each fuel was reformed to varying levels by adjusting the flow rates of air and fuel to provide differing fuel–air equivalence ratios. Additionally, the gas hourly space velocity was varied along with two different pressure conditions. The results from the natural gas test as a function of equivalence ratio at the lower pressure condition (15 psig) are shown in Figure 2. The results in Figure 2 show that the percentage of CO_2 and H_2O are relatively constant with varying equivalence ratio. However, as the equivalence ratio decreases



Figure 1. Test facility to reformat diesel, gasoline, and natural gas to varying level and determine their speciation using gas chromatography

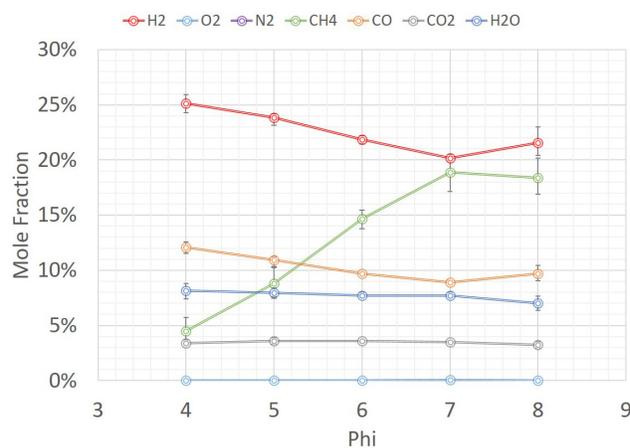


Figure 2. Natural gas reformat speciation at 15 psig

the fraction of unreacted methane decreases and the percentages of CO and H₂ increase.

Figure 3 shows the CFR engine where modifications were made to be able to characterize the autoignition properties of the reformat mixtures. In this first year of the project, the CFR engine was used to create a PRF mapping by autoigniting blends of n-heptane and isooctane in HCCI.



Figure 3. CFR engine with surrounding subsystems to create the PRF mapping using HCCI to determine the autoignition tendency of the reformat mixtures

Figure 4 shows the intake temperature requirements to autoignite different blends of n-heptane and isooctane at compression ratios (CR) ranging from 8 to 16. All of the data in Figure 4 was collected at 1,200 rpm and an equivalence ratio of 0.3. This mapping will now be used to determine an effective PRF number of each of the reformat fuels by autoigniting them under the same conditions (i.e., 1,200 rpm and equivalence ratio of 0.3) in HCCI combustion. Once the effective PRF number of each of the reformat fuels and the parent fuels have been determined, the candidate parent fuel–reformat pairs will be selected for testing in reformat RCCI.

Conclusions

- During the first year of the project, a test facility was constructed to reform gasoline, diesel, and natural gas.
- Modifications were made to a CFR engine and a PRF mapping was created at varying intake temperatures and compression ratios.
- The parent fuels were reformed and the constituent species of the reformat mixture were characterized.

References

1. Reitz, R., and Duraisamy, G., “Review of high efficiency and clean reactivity controlled compression

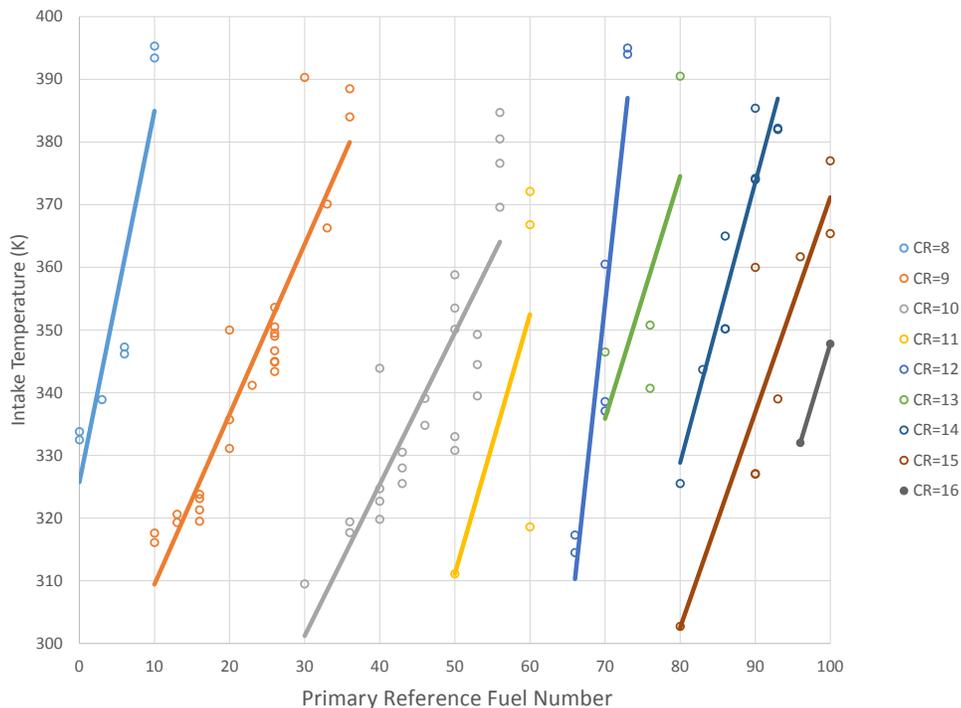


Figure 4. PRF mapping created using the CFR engine

ignition (RCCI) combustion in internal combustion engines,” *Progress in Energy and Combustion Science*, Volume 46, February 2015, Pages 12–71, ISSN 0360-1285.

2. Kokjohn, S., Hanson, R., Splitter, D., and Reitz, R., “Fuel Reactivity Controlled Compression Ignition (RCCI): A Pathway to Controlled High-Efficiency Clean Combustion,” *International Journal of Engine Research*, Special Issue, Vol. 12, pp. 209–226, 2011.
3. Curran, S., Gao, Z., and Wagner, R., “Reactivity Controlled Compression Ignition Drive Cycle Emissions and Fuel Economy Estimations Using Vehicle Systems Simulations with E30 and ULSD,” *SAE Int. J. Engines*, 2014.
4. Curran, S., Hanson, R., Wagner, R., and Reitz, R., “Efficiency and Emissions Mapping of RCCI in a Light-Duty Diesel Engine,” *SAE Technical Paper 2013-01-0289*, 2013.

VI.6 Reduced Petroleum Use Through Easily-Reformed Fuels and Dedicated Exhaust Gas Recirculation

Overall Objectives

- Quantify the impact of fuel chemistry and formulation on Dedicated Exhaust Gas Recirculation (D-EGR[®]) hydrogen production
- Optimize the operation of a D-EGR engine with purpose-developed fuel
- Demonstrate a >25% reduction in petroleum usage for a mid-sized passenger car

Fiscal Year (FY) 2016 Objectives

- Modify an existing research engine for operation as a D-EGR engine
- Characterize the impact of fuel delivery and valve phasing on hydrogen production
- Demonstrate increased hydrogen production with conventional fuel

FY 2016 Accomplishments

- Completed modifications to the research engine
- Demonstrated hydrogen production of 7% (vs. 3% reported in previous work)

Future Directions

- Evaluate the impact of petroleum fuel chemistry on hydrogen production
- Evaluate the impact of biofuel chemistry on hydrogen production
- Demonstrate an engine that will achieve a 25% petroleum use reduction relative to a baseline passenger car engine ■

Introduction

This project is focused on improving the efficiency of a gasoline engine by using advanced petroleum and bio-derived fuels in a Dedicated EGR engine. The D-EGR engine uses one or more of the cylinders to recirculate exhaust gas back to the intake of the engine. This increases the efficiency of the engine by itself, but also allows running those cylinders in such a way

Thomas E. Briggs, Jr. (Primary Contact), Terrence F. Alger, III

Southwest Research Institute[®] (SwRI)
6220 Culebra Road
San Antonio, TX 78238-5166
Phone: (210) 522-5153
Email: tbriggs@swri.org

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager:
Nicholas Damico

Subcontractors:

- Fiat Chrysler Automobiles, Auburn Hills, MI
- Total Specialties USA, Houston, TX

that they produce hydrogen as one of the byproducts of combustion. Hydrogen enhances combustion so that the compression ratio of the engine can be increased and so it can be optimized to run in a more efficient manner.

Running such an engine on regular gasoline provides significant benefits, but becomes limited in how much hydrogen can be produced due to fuel chemistry. By adjusting the chemistry of the fuel, an even more efficient version of the engine can be built which will support the DOE goal of a 25% improvement in vehicle fuel economy for a typical passenger car.

Approach

An existing engine will be modified to function as a D-EGR engine. The operation of the engine on gasoline will then be optimized to ensure that the fuel injection approach and intake and exhaust valve timings are optimal for producing hydrogen using a known fuel. The fuel chemistry will then be adjusted using a combination of refinery products which are already made (though potentially not used in gasoline) and bio-derived fuel products. The potential improvement in hydrogen production will be demonstrated using these fuels.

Results

An experimental campaign was conducted to evaluate the impact of intake valve phasing, exhaust valve phasing, fuel delivery approach, injection pressure, and injection timing. These studies were planned to fully consider the range of possible control that can be achieved on a typical gasoline engine using production-realistic hardware. The range of parameters are shown in Table 1.

Table 1. Independent Control Parameters of Interest Investigated for Maximum Reformate Production

Independent Variables	Authority
Intake valve phasing [°CA/2]	0–32
Exhaust valve phasing [°CA/2]	0–32
Fueling system	Direct injection (DI) – wall guided or port fuel injection (PFI)
Injection pressure [bar]	GDI: 20–200 – speed and load dependent PFI: 4
Injection timing [°bTDC]	Complete authority on injection timing, GDI: three strategies studied for simplicity – single early (310), split 50:50 (310, 230), single late (260) PFI: 200

°CA – degrees crank angle; °bTDC – degrees before top dead center; GDI – gasoline direct injection

The results of the studies investigating the impact of the above variables showed a significant increase in hydrogen production from the dedicated cylinder. Past results published by SwRI showed the maximum enrichment to be approximately 30–40% beyond stoichiometric operation. By optimizing the cylinder conditions and fuel delivery, nearly twice the previous level of enrichment was achieved, nearly doubling the hydrogen production. A summary of the results is shown in Figure 1. This plot shows enrichment and hydrogen production for both PFI injection and split GDI injection at three speed/load cases. The individual points for each fuel delivery system show the impact of valve phasing for each case.

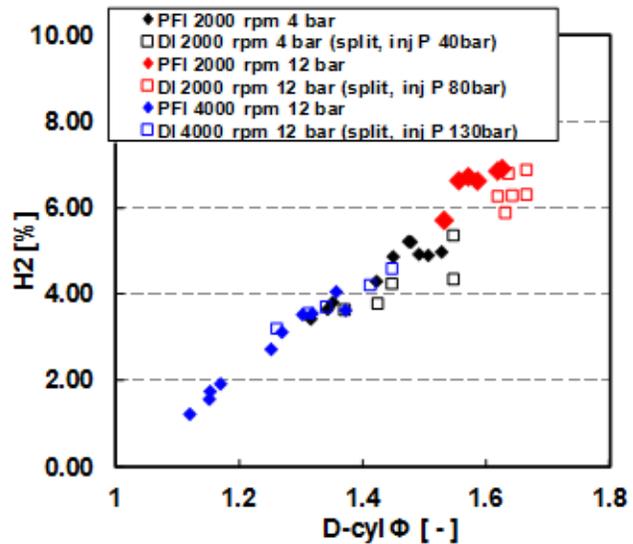


Figure 1. H₂ concentration in the wet exhaust from the dedicated cylinder expressed as function of dedicated cylinder (D-cyl) equivalence ratio for investigated speed-load conditions with PFI and 50:50 split DI strategies

Conclusions

The results from this phase of the project demonstrate that the combustion system can be optimized for significant increases in hydrogen production, but that there is still room to increase the hydrogen production before any physical, chemical, or other limits are reached. The expectation is that fuel chemistry will open the path to these increased hydrogen levels.

FY 2016 Publications/Presentations

1. Kalaskar, V., Gukelberger, R., Denton, B. and Briggs, T., “The Impact of Engine Operating Conditions on Reformate Production in a D-EGR Engine,” SAE Paper 17PFL-0457, *in press*.

VI.7 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) 2016 Objectives

- Blend a full boiling-range gasoline with single component, gasoline-representative molecules at 10% v/v levels, and characterize the chemico-physical properties of the blended fuels using Chevron's facilities
- Acquire autoignition delay and heat release measurements for the 10% v/v gasoline blends in Argonne's twin-piston RCM
- Acquire performance and emissions data for the 10% v/v gasoline blends using Argonne's prototype GCI engine
- Further develop correlations for the fundamental RCM measurements which can indicate operational performance within the GCI engine, and other LTC schemes

FY 2016 Accomplishments

- Blended a full boiling-range gasoline with 10 different single component, gasoline-representative molecules at 10% v/v levels, and characterized properties of the blended fuels using Chevron's facilities
- Acquired autoignition delay and heat release measurements for the 10% v/v gasoline blends in Argonne's twin-piston RCM
- Acquired performance and emissions data for the 10% v/v gasoline blends using Argonne's prototype GCI engine
- Further developed correlations for the fundamental RCM measurements which will indicate operational performance within the GCI engine

S. Scott Goldsborough (Primary Contact), Steve Ciatti

Argonne National Laboratory
9700 S. Cass Avenue
Bldg. 362
Argonne, IL 60439
Phone: (630) 252-9375
Email: scott.goldsborough@anl.gov

William Cannella

Chevron Energy Technology Company
100 Chevron Way
Richmond, CA 94801
Phone: (510) 242-2829
Email: bijc@chevron.com

DOE Technology Development Manager:
Kevin Stork

Future Directions

- Blend and characterize the properties of additional fuels at 20% v/v levels using single- and two-component surrogates using Chevron's facilities
- Acquire autoignition delay and heat release measurements for the 20% v/v blended gasolines using Argonne'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
- Based on experimental observations, formulate a measurement protocol which is capable of quantifying fuel sensitivities important for GCI (and other LTC modes) including temperature, pressure, equivalence ratio, and dilution, i.e., exhaust gas recirculation (EGR) ■

Introduction

There is substantial potential to utilize advanced LTC schemes to achieve improved fuel economy and engine-out emissions relative to conventional approaches to 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 mixedness, 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 EGR (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 Numbers (RON, MON, respectively) and cetane number. Alternative fuel quality metrics are needed which can account for the physical–chemical variations that can 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 is acquired using an RCM and a prototype GCI engine while reduced-order and detailed modeling are conducted to better understand fuel property impacts. The unique combination of the RCM and GCI engine datasets provides 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., $T = 600\text{--}1,100\text{ K}$, $P = 5\text{--}80\text{ bar}$) 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, and thermal and compositional stratification. Furthermore, the operating conditions, e.g., T , P , ϕ and O_2 , can be independently varied, unlike in an internal combustion engine, and this provides necessary insight. The ability to utilize wide ranges of fuel and oxygen concentrations within RCMs, from ultra-lean to over-rich (e.g., $\phi = 0.2$ 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. Argonne'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), but also operate with reduced levels of brake specific fuel consumption, especially at low- and mid-loads. Even compared to reduced power density Atkinson cycle engines, GCI engines have comparable or superior minimum brake specific fuel consumption. Recent improvements to hardware at Argonne, including reduced compression ratio pistons (15:1 rather than stock 17.5:1) and an 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 at highly boosted conditions under low speed operation [13].

Results

A baseline (California reformulated gasoline blendstock for oxygenate blending, regular-grade) gasoline fuel was blended with 10 different single-component, gasoline-representative molecules including n-heptane, iso-octane, toluene, 2-methyl-2-butene, methylcyclohexane, p- and o-xylene, ethanol, and n- and iso-butanol. These components cover hydrocarbon classes present in petroleum-derived gasoline, as well as potential future bio-derived fuels. The fuels' chemico-physical properties, including RON, MON, D86 distillation, net heat of combustion, and carbon and hydrogen content were determined using ASTM standardized testing protocol, while detailed hydrocarbon analyses were also conducted. The detailed hydrocarbon analyses 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. 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 RON values for the 10% v/v fuels ranged from 80 to 92, with sensitivities ($S = \text{RON} - \text{MON}$) from 1.5 to 8. Based on these results, it is projected that the 20% v/v fuels to be used in FY 2017 will cover $\text{RON} = 73\text{--}97$ with $S = 0\text{--}11$.

RCM tests conducted in FY 2015 using the baseline gasoline were extended in FY 2016 to cover conditions directly relevant to the thermodynamic and fuel loading conditions experienced in the GCI engine. For direct quantitative comparison, the GCI engine was operated using a very early fuel injection scheme, with all of the fuel injected just after intake valve closure. This “quasi-HCCI” approach ensured that the fuel–air charge was fairly well mixed by the time autoignition occurred, which is close to the premixed conditions used in the RCM. A sweep of intake temperature was conducted in the GCI engine where the intake pressure was adjusted in order to control or maintain the combustion phasing, as demarcated by the 10% heat release point (CA10). Mimicking the same compressed conditions as in the engine, it was found that a contour of constant ignition delay time, e.g., $\tau_{\text{RCM}} = 3$ ms, compared very favorably to the compressed conditions required in the engine to fix the CA10 point. This is illustrated in Figure 1.

Tests were further conducted in the GCI engine in order to develop a robust methodology whereby the influences of fuel concentration, or ϕ -stratification could be quantified. The intent of the measurements was to focus on autoignition tendencies, or ignition timing

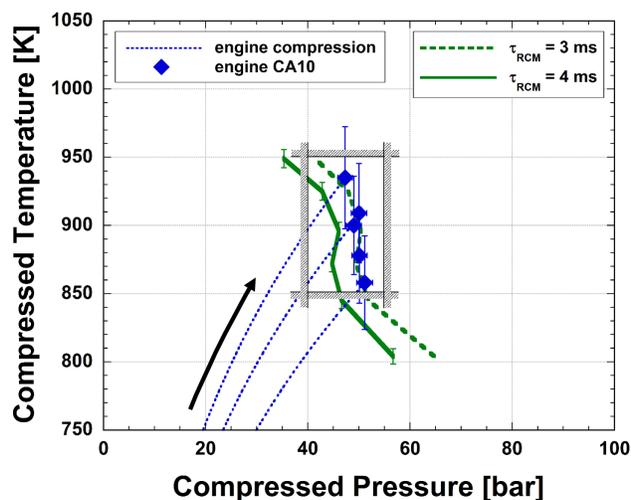


Figure 1. Comparison of compression histories for GCI engine operation (CA10 points are identified by blue diamonds), with RCM measurements where lines of constant ignition delay time are shown

shifts, as opposed to later stage combustion processes like soot burnout. In this way, the trends observed in the RCM measurements can be directly compared against those observed in the engine. Reactivity gradients, or ϕ -stratification can be generated in the GCI configuration via changes to fuel injection timing, fuel injection pressure, split injection, and/or swirl. A comprehensive series of measurements was undertaken using the baseline gasoline over a range of operating conditions in order to create the testing framework. Hardware constraints such as poor injector performance at low rail pressures, as well as spray interactions with the piston bowl were found to influence the measurements under some conditions.

Based on ongoing observations between the RCM and GCI engine data, a test protocol for the RCM was developed that should, for most all of the fuels in the test matrix, be able to systematically and reliably quantify influences of T , P , ϕ , and O_2 which would be experienced in an advanced compression ignition engine scheme, such as GCI or others. Initial tests were conducted with the baseline gasoline and most of the 10% v/v blends with the complete series planned for FY 2017.

In FY 2017 an intake air heater will be added to the GCI engine setup, while a smaller pulley will be fabricated for the supercharger. These modifications will significantly expand the operating capabilities of the engine, e.g. $T_{\text{in}} = 30\text{--}110^\circ\text{C}$ with P_{in} covering sub-ambient, throttled conditions to 1.7 bar, and allow the 20% v/v blended fuels, which will have significantly different autoignition characteristics to be characterized on a consistent basis.

Conclusions

- Argonne’s RCM has been used to acquire autoignition data for the full boiling-range, baseline gasoline, and 10% v/v blended fuels over a range of engine-relevant conditions, while the fuels were also utilized over a range of conditions in ANL’s prototype GCI engine.
- Direct comparisons between the RCM and GCI engine data have highlighted that under constant combustion phasing conditions good correlation is observed between the two experimental measurement platforms.
- A robust methodology has been developed to quantify ϕ -sensitivity with the GCI engine configuration though hard.

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/remworkshop>)
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.

FY 2016 Publications/Presentations

1. K. Cung, T. Rockstroh, S. Ciatti, W. Cannella, S.S. Goldsborough, "Parametric study of ignition and combustion characteristics from a gasoline compression ignition engine using two different reactivity fuels," ICEF 2016-9395, 2016.

VI.8 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) 2016 Objectives

- Develop optimized combustion system options for in-cylinder gasoline/compressed natural gas (CNG) blending concept using validated modeling approach
- Select promising hardware options based on pre-determined evaluation criteria and design feasibility study
- Experimentally validate the performance of the optimized configurations

FY 2016 Accomplishments

- Successfully designed and implemented increased compression ratio engine options and injector nozzle design based on three-dimensional (3D) computational fluid dynamics (CFD) modeling results
- Demonstrated 40.9% indicated efficiency with NG direct injection at 12.5:1 compression ratio (CR), exceeding the efficiency in gasoline PFI operation by 11.9%, an ~41% relative improvement
- Validated blending concept potential to improve power density achieving an increase in indicated mean effective pressure (IMEP) from 5.8 bar with E10 (10% ethanol, 90% gasoline blend) to 10.2 bar with NG, a relative improvement of more than 75% taking advantage of the high knock resistance of NG at an increased CR of 12.5:1

Future Directions

- Implement efficiency and performance characteristics from optimized hardware configurations in the vehicle level analysis

Thomas Wallner (Primary Contact), Michael Pamminger, Riccardo Scarcelli, James Sevik

Argonne National Laboratory
9700 S. Cass Avenue
Lemont, IL 60439
Phone: (630) 252-3003
Email: twallner@anl.gov

Ronald Reese, Asim Iqbal

FCA US LLC
1000 Chrysler Drive
Auburn Hills, MI 48326
Phone: (248) 576-5022
Email: Ron.Reese@fcagroup.com

Steven Wooldridge, Brad Boyer

Ford Motor Company
2101 Village Rd
Dearborn, MI 48124
Phone: (313) 248-7003
Email: swooldri@ford.com

DOE Technology Development Manager:
Kevin Stork

- 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 U.S. 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 NG, 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 diagnostics 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 ensure 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 an NG direct injection 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

Assessment of Optimized Combustion System Options for In-Cylinder Blending Concept

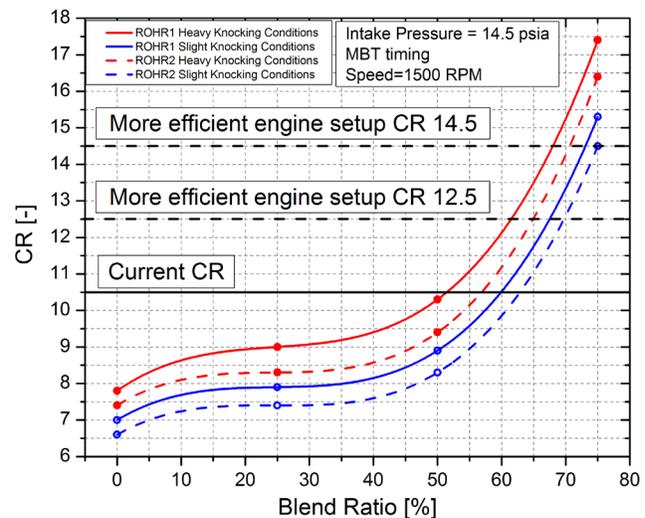
Mixture homogeneity as well as in-cylinder turbulence were determined to be the most relevant quantitative evaluation criteria to identify promising configurations and operating strategies for optimized in-cylinder gasoline/CNG blending concepts. Therefore, these two

metrics were used to objectively evaluate the potential of proposed design variants via 3D-CFD simulations.

The first design variation focused on optimizing the CR of the engine. Two discrete steps in CR above the baseline of 10.5:1 were selected, with the maximum CR limited by physical constraints such as piston interference. CRs of 12.5:1 and 14.5:1 were determined feasible with the higher of the two CR options intended to result in operation near the knock limit with neat natural gas as the fuel (Figure 1). The graph also shows that at least 50% NG and ~60% NG were required to mitigate heavy knock conditions for CR 10.5:1 and 12.5:1 at wide open throttle, respectively.

While a CR of 12.5:1 can be achieved with the same piston as the 10.5:1 CR baseline case by reducing the squish height, a piston with a build-up was designed and manufactured for the 14.5:1 case. The 14.5:1 piston design minimizes the required build-up while maintaining constant squish height compared to the 12.5:1 CR case with the baseline piston. Figure 2 shows a design of the baseline piston (left), the high CR piston (middle) as well as a photograph of the machined piston (right).

Improving in-cylinder charge motion has shown to be an effective means for increasing dilution tolerance. Within the scope of this project increased charge motion was generated by using two different methods – by changing the intake charge motion and by inducing charge motion with the direct injection event. The effect of in-cylinder charge motion was assessed by changing the in-cylinder



MBT – maximum brake torque; ROHR – rate of heat release

Figure 1. Prediction of knock-limiting CR as a function of gasoline/CNG blend ratio

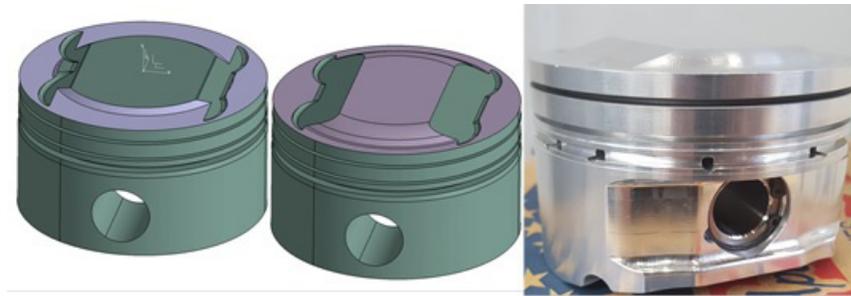


Figure 2. Piston designs for baseline (left), increased CR (middle), and machined piston with buildup (right)

tumble. Tumble plates in the intake runners were evaluated as a way to increase the tumble relative to the baseline configuration. Two tumble ratios, a baseline as well as high tumble case, were evaluated at part-load operating conditions. It was found that the interaction of the gaseous jet with the intake induced flow played a key role. The gaseous jet can reduce or increase the tumble, especially for the configuration with the injector in side location. Injector jet characteristics are another lever influencing charge motion. Within the scope of this project the injector jet characteristics were altered by modifying the outward opening injector to resemble typical characteristics of an inward opening injector allowing for asymmetric jet configurations. Inserts with different hole configurations were designed and evaluated using the validated 3D-CFD modeling approach. Figure 3 shows the detailed mesh of a three-hole configuration, location and orientation of the injector insert inside the combustion chamber, as well as the machined hardware that was used for the experimental assessment.

A detailed 3D-CFD modeling analysis was performed for a multitude of combinations of potential optimized hardware configurations. Variables that were evaluated in simulation included injector location and design, injection timing, charge motion as well as CR. Figure 4 shows example results of the modeling design study evaluating the impact of injector location, injector design, as well as

injection timing on in-cylinder turbulence combined with low and high tumble. As can be seen, a three-hole nozzle design with 45° hole angle mounted in central location results in increased in-cylinder charge motion compared to other configurations. For the NG injection event, two critical injection timing options were identified: an early injection timing (start of injection [SOI] 240° crank angle [CA] before top dead center) during the intake process that led to peak efficiency and an injection timing after intake valve closure (SOI 120°CA before top dead center) which resulted in a faster combustion process.

Experimental Evaluation of Optimized Hardware Configurations

Based on extensive modeling design evaluations, a limited number of hardware configurations were selected for experimental evaluation. The evaluation was focused on demonstrating the benefits of the in-cylinder blending while also evaluating its practical limits. The test matrix for the optimized configurations included high and low tumble levels, side and central injector location with and without the injector insert in central location, as well as three different CRs.

Figure 5 shows the results of spark sweeps that were performed at wide open throttle (WOT) conditions evaluating the impact of CR and fuel blend ratio on knock intensity (using a knocking intensity [KI] limit of 1 bar).

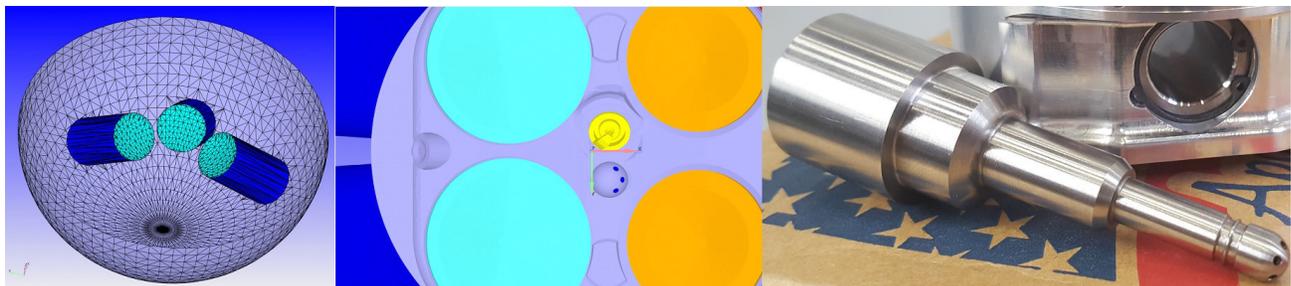
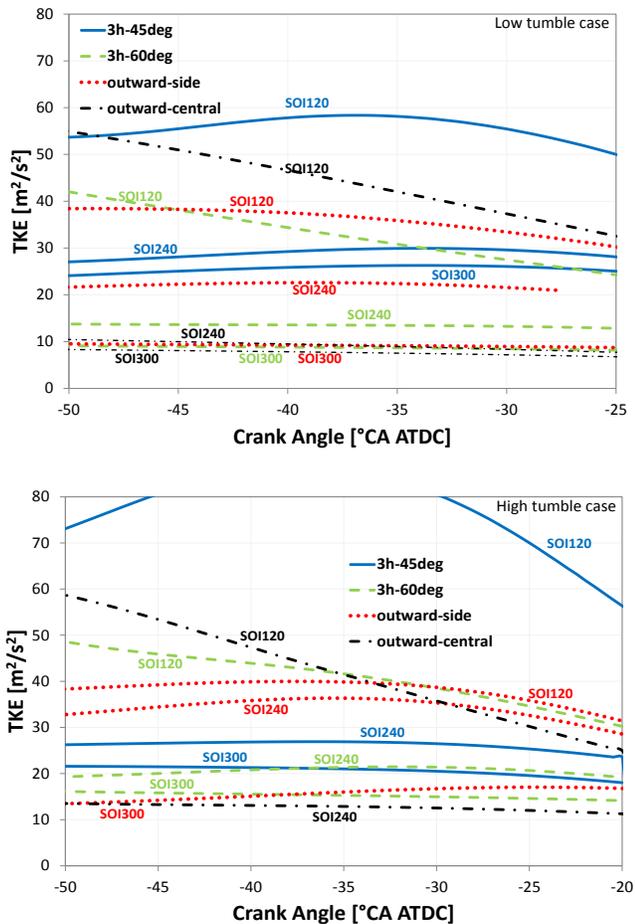


Figure 3. Meshing details and installation study of nozzle tip variant, with machined hardware

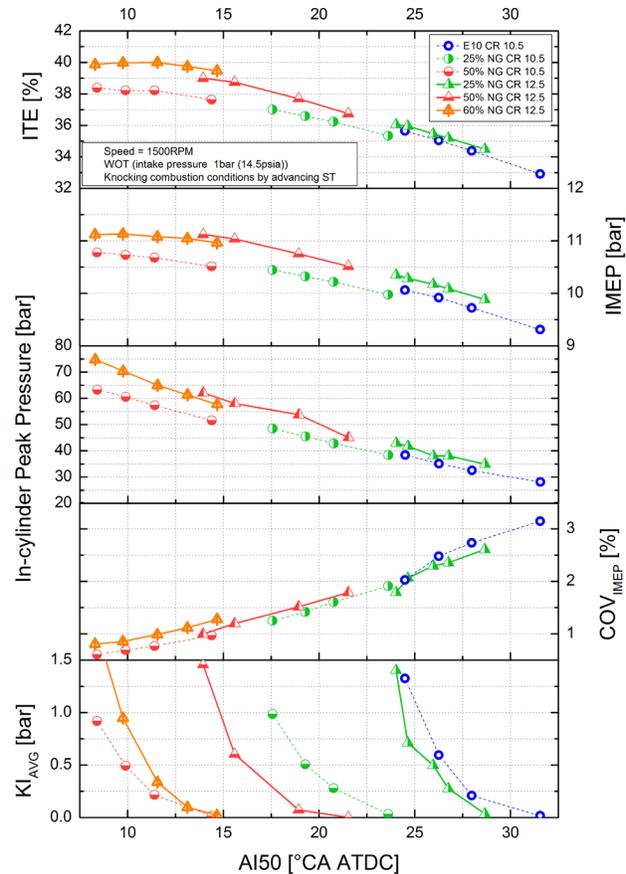


ATDC – after top dead center

Figure 4. Influence of intake design (top: low tumble, bottom: high tumble) on in-cylinder turbulent kinetic energy (TKE) for different injector configurations and injection timings

Optimal combustion phasing (AI50 [location of 50% burn] around 8°CA ATDC) could be maintained with a 50% blend at a CR of 10.5:1 while a 60% NG blend was required to achieve optimal phasing at 12.5:1 CR. The experimental results also validated the model predictions of the required blend ratio for a given CR (see Figure 1).

Figure 6 shows a comparison of efficiency maps for a CR of 12.5:1 with E10 PFI (left) and NG direct injection (DI) with the injector in side location (right). Both cases were operated with low tumble typical of gasoline port fuel injected engines. The high knock resistance of natural gas combined with DI allowed for a significant improvement in WOT performance as well as dramatic improvements in efficiency in the mid and high load region. While applying the in-cylinder blending concept to the baseline engine configuration with 10.5:1 CR resulted in a 17.8% relative efficiency improvement at 1,500 rpm and full load [2],



ITE – indicated thermal efficiency; ST – spark timing;
 COV_{IMEP} – coefficient of variation in indicated mean effective pressure

Figure 5. Experimental assessment of knock limits as a function of CR and blend ratio

employing the engine hardware optimized for this concept with increased CR resulted in a relative improvement in efficiency of almost 24% while improving power density by almost 20% relative to operation with E10 at 1,500 rpm. Even more significant improvements in power density were attainable at lower engine speeds where engine knock limits operation with E10 to 5.8 bar IMEP at 1,000 rpm while 10.2 bar IMEP was achieved with NG direct injection. At an engine speed of 2,000 rpm, the attainable indicated efficiency at WOT conditions was increased from 29% with E10 to 40.9% with NG DI while increasing engine load by almost 1.7 bar IMEP.

Conclusions

This project was designed to evaluate the potential benefits of targeted in-cylinder blending of NG with gasoline and has successfully met all second year milestones. Specific FY 2016 accomplishments include:

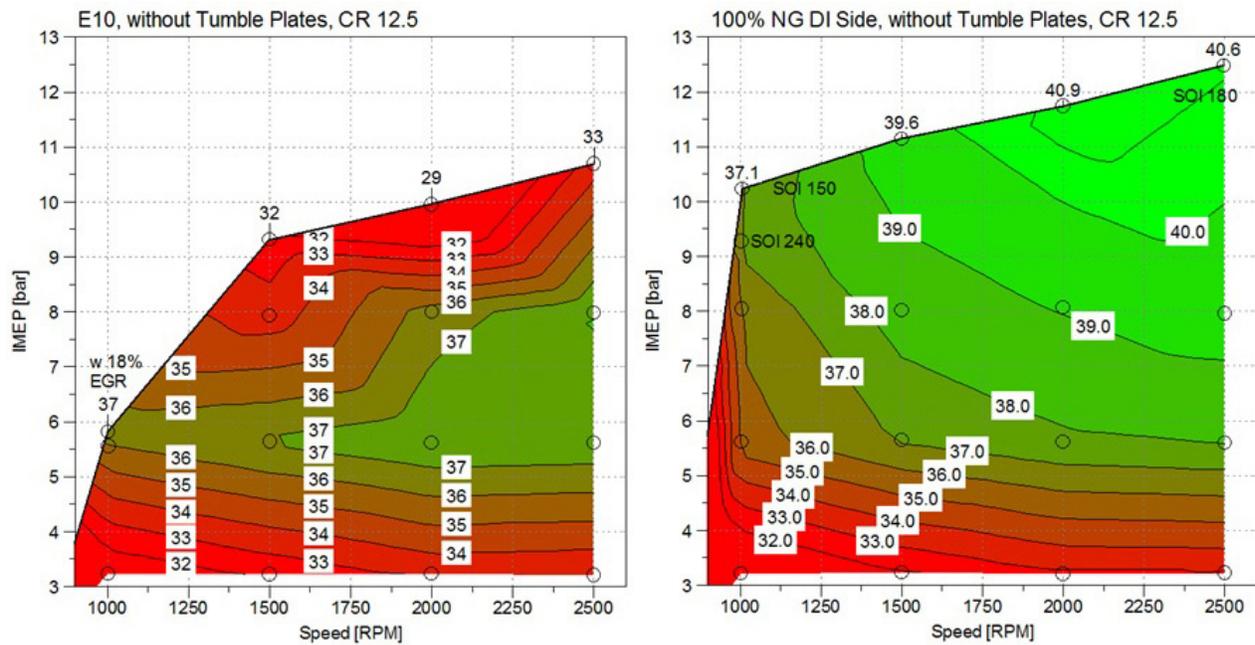


Figure 6. Comparison of efficiency maps for E10 PFI (left) and NG DI (right) at 12.5:1 CR

- Successfully designed and implemented increased compression ratio engine options and injector nozzle design based on 3D-CFD modeling results
- Demonstrated 40.9% indicated efficiency with NG DI at 12.5:1 CR, exceeding the efficiency in gasoline PFI operation by 11.9%, an ~41% relative improvement
- Validated blending concept potential to improve power density achieving an increase in IMEP from 5.8 bar with E10 to 10.2 bar with NG, a relative improvement of more than 75% taking advantage of the high knock resistance of NG at this increased CR

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. Vehicle Technologies Office: Fuel and Lubricant Technologies 2015 Annual Progress Report.
3. Bartolucci, L., Scarcelli, R., Wallner, T., Swantek, A. et al., "CFD and X-Ray Analysis of Gaseous Direct Injection from an Outward Opening Injector," SAE Technical Paper 2016-01-0850, 2016, doi:10.4271/2016-01-0850.
4. Wallner, T., Pamminger, M., Sevik, J., Scarcelli, R., Wooldridge, S., Boyer, B., "Performance and Efficiency Potential of an Engine Concept employing NG Direct Injection and In Cylinder Fuel Blending with Gasoline," 11th Conference on Gas-Powered Vehicles: Gaseous-Fuel Drives and Climate Protection Targets: The Right Path. Potsdam, Germany. 2016.
5. Pamminger, M., Wallner, T., Sevik, J., Scarcelli, R., Hall, C., Wooldridge, S., Boyer, B., "Performance, Efficiency and Emissions Evaluation of Gasoline Port-Fuel Injection, Natural Gas Direct Injection and Blended Operation," ASME 2016 Internal Combustion Engine Fall Technical Conference. Greenville, SC, 2016.
6. Sevik, J., Pamminger, M., Wallner, T., Scarcelli, R. et al., "Influence of Injector Location on Part-Load Performance Characteristics of Natural Gas Direct- Injection in a Spark Ignition Engine," SAE Int. J. Engines 9(4):2016, doi:10.4271/2016-01-2364.
7. Pamminger, M., Sevik, J., Scarcelli, R., Wallner, T. et al., "Evaluation of Knock Behavior for Natural Gas - Gasoline Blends in a Light Duty Spark Ignited Engine," SAE Int. J. Engines 9(4):2016, doi:10.4271/2016-01-2293.

FY 2016 Publications/Presentations

1. Sevik, J., Pamminger, M., Wallner, T., Scarcelli, R. et al., "Performance, Efficiency and Emissions Assessment of Natural Gas Direct Injection compared to Gasoline and Natural Gas Port-Fuel Injection in an Automotive Engine," SAE Int. J. Engines 9(2):2016, doi:10.4271/2016-01-0806.

7. Hall, C., Sevik, J., Pamminger, M., Wallner, T.,
“Hydrocarbon Speciation in Blended Gasoline-Natural
Gas Operation on a Spark-Ignition Engine,” SAE 2016
International Powertrain Fuels & Lubricants Meeting.
Baltimore, MD, 2016.

VI.9 High-Efficiency Cost-Optimized Spark-Ignited Natural Gas (HECO-SING) Engines

Overall Objectives

- Develop and demonstrate a High-Efficiency Cost-Optimized Spark-Ignited Natural Gas (HECO-SING) heavy-duty engine capable of approaching current near-diesel efficiency while achieving current Environmental Protection Agency emission regulations
- Increase engine efficiency through optimized dilution with both exhaust gas recirculation (EGR) and excess air
- Key enablers:
 - Advanced ignition system for robust combustion with high dilution
 - Lean capable exhaust aftertreatment
 - Advanced engine and aftertreatment controls (passive selective catalytic reduction [SCR])
- Targets:
 - Environmental Protection Agency 2017 on-highway emissions
 - Peak brake thermal efficiency >42%

Fiscal Year (FY) 2016 Objectives

- Convert engine to an EGR lean burn and stoichiometric capable system
- Quantify baseline engine performance and emission levels
- Begin initial engine system development studies
- Perform ignition system literature review study
- Select advanced ignition systems from the literature review to be used in the project
- Perform catalyst literature review study
- Begin aftertreatment model development
- Acquire catalyst samples to be tested and quantified to the model

Alex Freitag (Principal Investigator), Steve White (Project Manager, Primary Contact)

Robert Bosch LLC
38000 Hills Tech Dr.
Farmington Hills, MI 48331
Phone: (248) 876-1421
Email: steve.white@us.bosch.com

DOE Technology Development Manager:
Kevin Stork

NETL Project Manager:
Chuck Alsup

Subcontractors:

- Volker Sick and Michael Gross, University of Michigan, Ann Arbor, MI
- Mark Stewart, Pacific Northwest National Laboratory (PNNL), Richland, WA

FY 2016 Accomplishments

- Performed baseline testing on as-received lean burn non-EGR configured engine
- Initial studies on level of ammonia generation in varied rate EGR and non-EGR configurations, critical to assess feasibility of passive SCR concept, performed
- Project baseline testing performed on engine converted to stoichiometric EGR configuration (representing current state-of-the-industry)
- Detected issues with the original turbocharger sizing and EGR system implementation, and revised design to operate successfully
- Ignition systems literature review study performed, completed, and presented to DOE representatives
- Selection of advanced ignition systems to study on the engine accomplished (conventional higher energy ignition, constant energy ignition, corona discharge, and turbulent jet ignition)

- Combustion optical instrumentation designed fabricated (see Figure 1)
- Combustion optical and spectroscopic in-cylinder measurement system device and accessories specified and procured
- Bench top rig created to assess optical measurement capabilities and pre-preparation for engine testing, to quantify ignition systems combustion impacts
- Began aftertreatment model development
- Identified and included capturing of engine hydrogen output levels over the range of operation for input into the aftertreatment model, which was not originally identified in the project submission
- Catalyst literature review study performed and completed
- Initial conventional ignition systems combustion limit study performed
- Initial assessment of passive SCR (manual mode) engine efficiency performed
- Analyze effectiveness of aftertreatment model via testing on synthetic gas bench
- Develop software controls to allow for optimized switching between lean, rich, and stoichiometric operation for passive SCR function
- Verification of aftertreatment modeling, engine controls to achieve optimized efficiency and emissions operation, and ignition and fuel systems to achieve those improvements will be performed in the final budget year period ■

Future Directions

- Evaluation of the selected advanced ignition systems, assess their impact on combustion through performance and optical measurements, and assess their improvement on engine efficiency
- Present catalyst literature review study to DOE representatives at PNNL site visit
- Site visit to Bosch to witness combustion measurements on engine

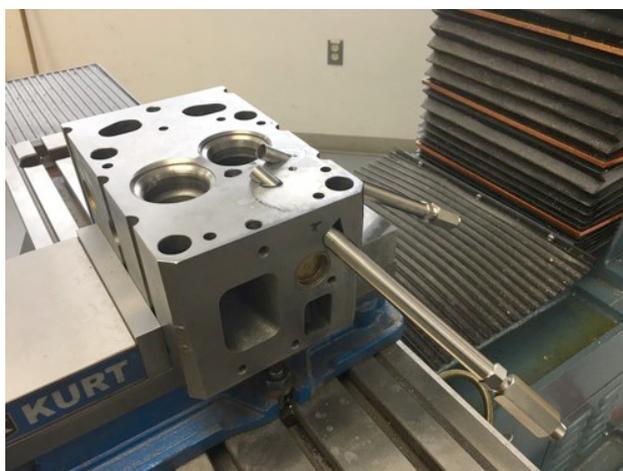


Figure 1. Cylinder head optical probe configuration

Introduction

The abundance of relatively low cost natural gas in the North American market, along with energy independence, makes natural gas attractive as an alternate fuel. Natural gas also has an advantage over diesel engines in low NO_x emissions production. Natural gas does however have some technical challenges in its lower efficiency due spark ignited homogeneous combustion in comparison to diesel or gasoline, which is also a partial factor in its vehicle storage capacity and thus driving range.

In order to address these challenges, the HECO-SING project was undertaken. The goal was to increase engine efficiency (fuel economy), while still meeting future emissions, in a cost-effective manner. In order to achieve these goals, high dilution combustion will be used with a focus on advanced ignition systems, optimized aftertreatment selection, and creative engine controls are applied.

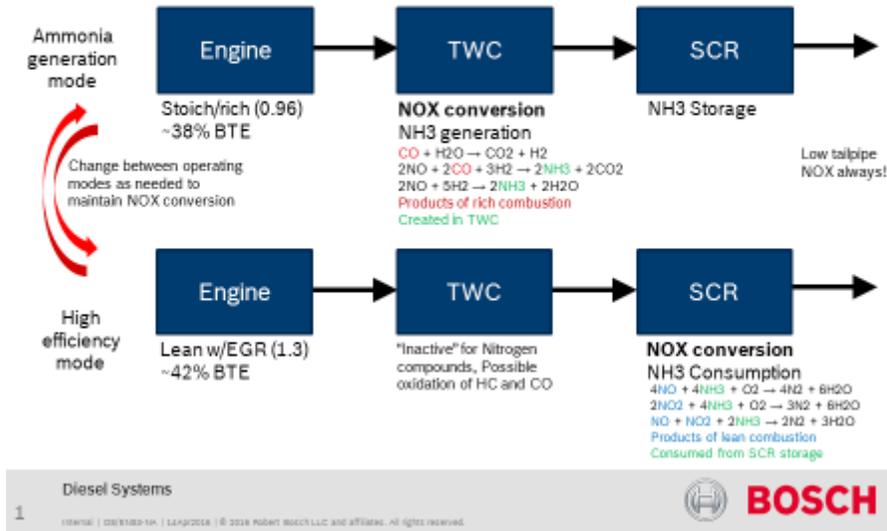
Approach

In order to maintain the low cost objective for this project, a passive SCR approach was undertaken, to reduce costs of the more expensive active SCR aftertreatment method. To achieve the passive SCR technique, a control strategy switching between a rich operating mode to generate NH_3 (ammonia) in the exhaust system rather than a complex and costly Diesel Exhaust Fluid (urea) dosing, and lean operation to increase engine operating efficiency (lower fuel consumption), was pursued. Optimum balancing of operation in the different operating modes to achieve increased efficiency while maintaining low emissions is the objective. See Figure 2 for an illustration of the operating mode functions.

To achieve the highest efficiency, utilizing advanced ignition systems which could extend the dilution limit boundary is investigated. Table 1 shows the comparison of different ignition systems and the ones selected for this study. The ammonia generation mechanism to decompose

HECO-SING Project Update

Passive SCR components, reactions and control concept



BTE - brake thermal efficiency; TWC - three-way catalyst; HC - hydrocarbon

Figure 2. Passive SCR concept

Table 1. Advanced Ignition Systems Recommendation

Approach	System	Ignition Characteristics					Flame Enhancement			Economic Factors	
		Energy Delivered(mJ)	Apex, Total Duration(ms)	Volume/Ignitable	Low Temperature	Pressure Tolerance	Efficiency	Early Growth	Mass Burn Rate	Durability	Low Cost
Conventional	Inductive Discharge	30 (0)	1	0	0	0	0	0	0	0	0
	Capacitive Discharge	55 (0)	0.1	0	0	0	+	0	0	0	0
High Energy, Low Volume	Dual-coil	55-360 (+)	1-3	0	0	+	? (0)	+	+	-	? (-)
	Bosch CCI	50-300 (+)	1-3	0	0	+	? (-)	+	+	? (-)	0
High Power, Low Volume	Breakdown	50 (0)	10 ⁶	0	-	+	++	+	0	-	0
	Laser	50-400 (+)	10 ⁷	0	-	+	++	+	0	?	? (-)
High Volume, Conventional	Multi-plug	50n (+)	1	++	0	+	0	+	++	-	---
	Rail-plug	2500 (++)	0.2	+	0	0	-	+	+	---	0
Non-Equilibrium Plasma	Microwave Assisted	50 (0)	2.5	0	+	-	+	+	+	? (-)	? (-)
	Corona	4000 (++)	0.5	++	+	? (-)	++	++	+	? (0)	? (-)
	no-pulsed Plasma	500 (+)	0.5-2	+	+	? (-)	++	++	+	? (0)	? (-)
High Momentum Jets	Turbulent Jet	+++	1-5	+++	?	+	?	+	++	? (-)	---
	Supersonic Jet	+++	1	+++	-	+	?	+	++	? (-)	? (-)
	Diesel Pilot	++	5	+++	0	++	?	+	++	-	---

0: No big effect
 -: Disadvantage
 ? : Our expectation
 +: Advantage
 ?: Unknown

4

the NO_x created while operating in the lean mode will be developed through exhaust gas simulation performed by PNNL. EGR is utilized to minimize NO_x while assisting in combustion stability to further expand the combustion dilution operating range. The balance of all parameters and operating conditions for best overall operations to meet project goals is paramount.

Results

Since the engine selected for this project was a dedicated natural gas engine, but configured for lean burn operation, conversion to also be capable of stoichiometric operation and EGR was necessary. Baselines in both the as received and stoichiometric with EGR configurations were performed. In order to provide access for the combustion optical measuring equipment as part of the ignition study, the turbocharger was relocated from an end mount design to a center mount on the engine. During initial testing in the converted configuration, it was determined the original turbocharger and EGR systems would not be adequate to achieve the desired results, so a revised design was implemented.

The original turbocharger configuration was to reuse the turbocharger from the as-received engine. This proved to be incorrect sizing for stoichiometric combustion, and resulted in insufficient backpressure for the desired EGR rates. The initial EGR design pulled EGR off of only one scroll from the dual-scroll turbocharger for design simplicity. Each scroll feeds three of the engines six

cylinders. This resulted in three of the cylinders having higher backpressure than the other three and thus higher residual EGR, causing higher combustion variability in those cylinders for a given external EGR rate. To rectify this conditions, a turbocharger was matched to the application with more suitable sizes for both the turbine and compressor, and the EGR system was reconfigured to provide EGR from both scrolls of the turbocharger. While a slightly more complex and costly system, the revised turbocharger and EGR system addressed all of the former designs limitations, and provided a higher external EGR rate, and thus power output, along with balancing the combustion variability between cylinders (see Figure 3). The baseline emissions results from the 13-mode test are shown in Table 2. In Figures 4–6, the different exhaust systems are shown illustrating the reconfiguration from lean burn to the first and final EGR systems.

To assist in the inputs to the model for the exhaust gas simulation, which is crucial in determining the operating mode strategy, engine measurements were made in the full range of operating conditions to obtain exhaust constituent output. Key inputs for the simulation for this type of control methods are hydrogen and ammonia levels. Since the catalyst literature review netted very little information on exhaust formation in a natural gas application, the actual engine data was critical for a successful model to be built.

Ammonia generation levels were pleasantly higher than anticipated with operating in that mode based on

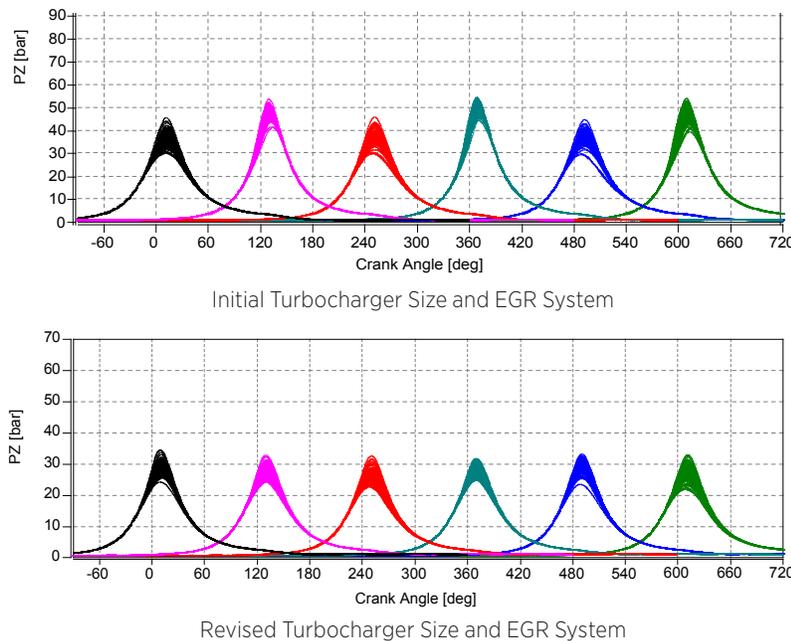


Figure 3. Combustion stability

Table 2. Baseline Engine Results

	HC [g/bhph] (CP)	CO [g/bhph] (CP)	NOX [g/bhph] (CP)	CO2 [g/bhph] (GHG)	BSFC [g/bhph] (Efficiency)	BSFC [g/kWh] (Efficiency)
WP10NG Stoich w/EGR baseline (TP)	0.70 THC	6.7	0.016	500	165	221
US 2017 HHDD Standard (TP)	0.14 NMHC	14.4	0.200	460		
WP10NG Lean w/o EGR, no ATS (EO)	5.0 THC	3.4	13.2	440		

BSFC – bracke specific fuel consumption; THC – total hydrocarbon; NMHC – non-methane hydrocarbon; TP – tailpipe; HHDD – heavy heavy-duty diesel; EO – engine-out; CP – criteria pollutant; GHG – greenhouse gas; ATS – aftertreatment system; WP10NG – Weichai Power 10-L natural gas engine



Figure 4. Baseline engine configuration

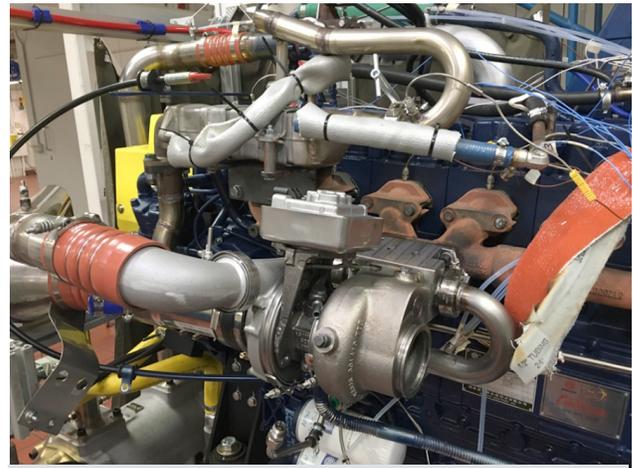


Figure 6. Revised turbocharger size and EGR system engine configuration



Figure 5. Initial turbocharger size and EGR system engine configuration

published data from gasoline engines. There is developing optimism that this technique might be successful for natural gas. Levels of ammonia generation in relation to EGR rate was performed. A predictable and linear level of ammonia versus EGR level was quantified, providing for a multi-dimensional level of adjustability in selecting operating modes to hopefully meet stated objectives. Ammonia generation levels can be seen in Figures 7 and 8.

Hydrogen is not a normal exhaust constituent that is measured through the course of normal development at Bosch on engine programs. A method to do so was then required. Through research, a device produced by H-Sense was determined to be the best commercial available product to utilize. Due to the specialized nature of the need for this measurement, purchasing a unit for just this project was not practical. Contact with Bosch technical centers in other regions indicated that the development center in Germany had one we could rent,

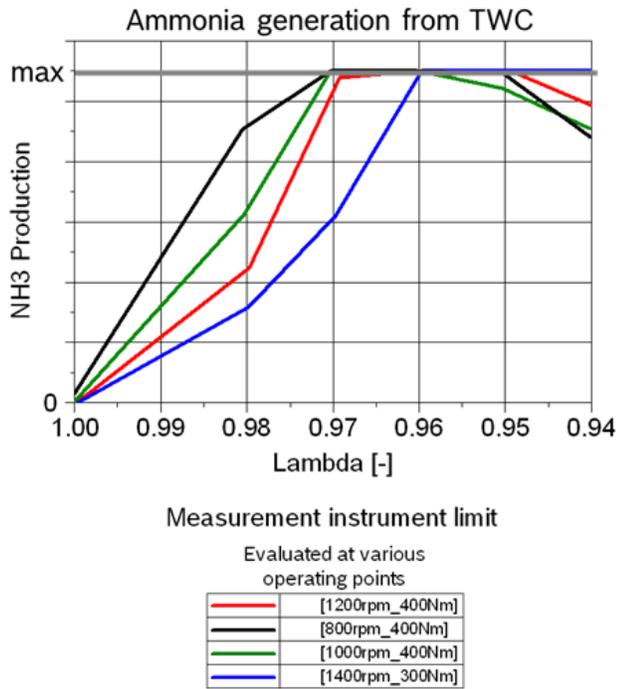


Figure 7. Ammonia generation – NH₃ vs. lambda

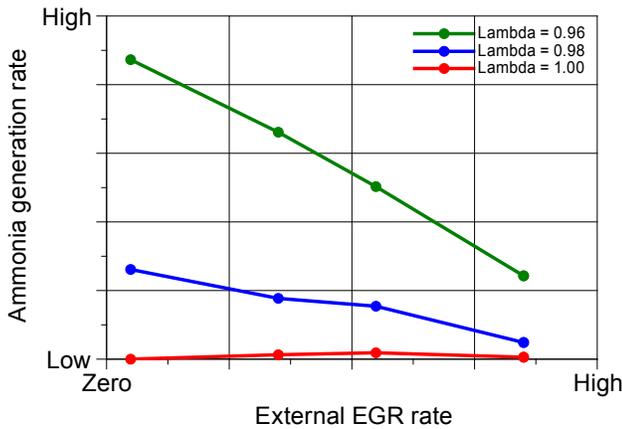
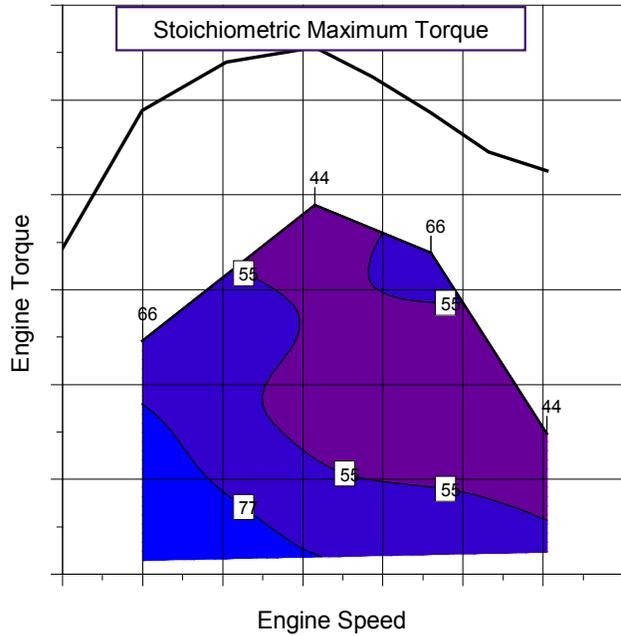


Figure 8. Ammonia generation – NH₃ vs. EGR

but the cost and timing were prohibitive for this project. Further discussions with our project partners determined that the University of Michigan had a unit that had been unused for many years and was available for loan to use if we could perform all the maintenance and prove out to get it operational. This proved to be the optimal solution and enabled us to gather the H₂ data needed to be provided to PNNL for their model development. Measurement of the engine-out hydrogen revealed that it is only dependent on engine air–fuel ratio, while the ammonia production rate of the TWC is dependent on other parameters as well as hydrogen, justifying the need for a physics-based model.



► Subset of overall speed-load map where lean and EGR operation is stable with 65mJ ignition coils

► Dilute homogeneous combustion improves BSFC compared to stoichiometric (on average 1.5 lambda and 9-11% EGR at points represented here)

Figure 9. Initial passive SCR potential gains: percent improvement in BSFC when running in lean + EGR mode vs. stoichiometric

In searching for the dilution boundary level that could be successfully operated with generally accepted current ignition systems, testing was performed with production Bosch 65 mJ ignition coils. Successful identification of boundary level was achieved, which will serve as a baseline. This data can be seen in Figure 9 along with the conceptual improvement with advanced ignition in Figure 10.

Conclusions

During this period, it was concluded that the concept of running rich through a TWC will generate high levels of ammonia that can be used in an SCR catalyst for lean NO_x reduction without a Diesel Exhaust Fluid system. Also, the improved efficiency of lean combustion and the engine-out NO_x levels were also characterized. The challenge remains to determine if the proper balance between the lean high-efficiency operating mode and rich

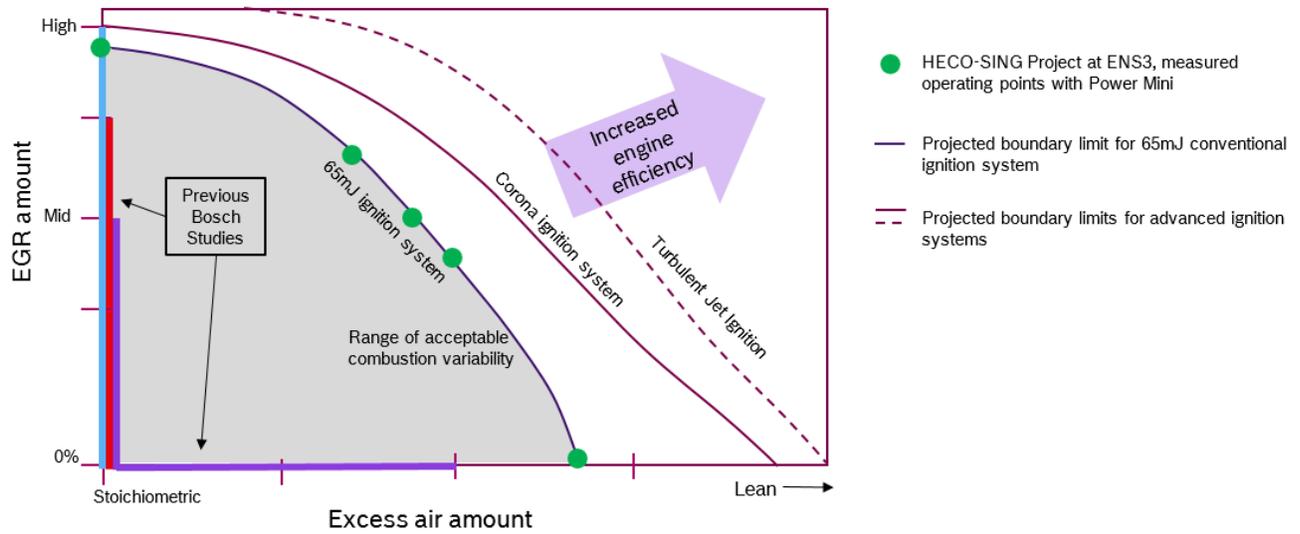


Figure 10. Ignition systems boundary limits, conceptual

ammonia-generation mode will be able to provide the overall project goals.

FY 2016 Publications/Presentations

1. Ignition system literature review poster presentation poster at the Michigan Institute for Plasma Science and Engineering (MIPSE) Graduate Symposium, October 2016.
2. Ignition system literature review poster presentation poster at the UM Engineering Graduate Symposium, November 2016.

VII. Index of Primary Contacts

A

Ajayi, Oyelayo192

B

Bays, Tim122, 231

Briggs, Jr., Thomas E.....247

C

Ciatti, Stephen.....78

Cosimbescu, Lelia.....218, 223

Curran, Scott.....90

D

Dec, John E.84

Demas, Nicholas G.179

F

Fenske, George184

Fioroni, Gina.....70, 107

G

Gangopadhyay, Arup K.144, 149

Goldsborough, S. Scott113, 135, 249

H

Hsu, Stephen.....159

K

Kocher, Lyle234

Kolodziej, Christopher P.33, 46

L

Lawler, Benjamin243

M

McNenly, Matthew	116
Mueller, Charles J.	100
Musculus, Mark P.B.	95

P

Pitz, William J.	127, 131
-----------------------	----------

Q

Qu, Jun	202, 213
---------------	----------

R

Ratcliff, Matthew A.	55
---------------------------	----

S

Sjöberg, Magnus	27, 41
Sluder, Scott	38, 228
Splitter, Derek	197
Storey, John M.E.	61, 209
Szybist, James P.	50

T

Toops, Todd J.	65
---------------------	----

W

Wallner, Thomas	253
Wang, Q. Jane	166
White, Steve	259
Wooldridge, Margaret S.	237
Wu, Gefei	174

Z

Zhao, Bin.	153
Zigler, Bradley T.	138

VIII. Project Listings by Organizations

Argonne National Laboratory

II.2	Studies of Research Octane Number (RON) and Heat of Vaporization (HoV)	33
II.5	Fuel Effects on EGR and Lean Dilution Limits on SI Combustion	46
III.1	Investigation on the Combustion of Selected High RON (Co-Optima) Fuels under GCI Operating Conditions	78
III.7	Small Volume Autoignition Tester	113
IV.4	Kinetic Mechanism Development and Validation	135
V.7	Lab-Engine Prediction and Correlation	179
V.8	Engine Friction Reduction Technologies	184
V.9	Phenomenological Modeling of Lubricant Film Formation and Performance	192
VI.7	GCI Metrics	249
VI.8	Efficiency-Optimized Dual-Fuel Engine with In-Cylinder Gasoline/CNG Blending	253

Cummins Inc.

VI.3	E85/Diesel Premixed Compression Ignition (EDPCI)	234
------	--	-----

Ford Motor Company

V.1	Development of PAG (Polyalkylene Glycol)-Based Lubricant for Light- and Medium-Duty Axle Applications	144
V.2	Power Cylinder Friction Reduction Through Coatings, Surface Finish, and Design	149

George Washington University

V.4	Integrated Friction Reduction Technology to Improve Fuel Economy without Sacrificing Durability	159
-----	---	-----

Lawrence Livermore National Laboratory

III.8	The Microliter Fuel Ignition Tester (uFIT): Creating a High Throughput Measurement Process for Small Sample Volumes	116
IV.2	Fuel Property Blending Model	127
IV.3	Kinetic Mechanism Development	131

National Renewable Energy Laboratory

II.7	Extension of the Particulate Matter Index (PMI) for Gasoline Blended with Oxygenates	55
II.10	Heat of Vaporization Measurement and Engine Knock Limit Effects	70
III.6	Small Volume Fuel Autoignition Tester Development	107
IV.5	Kinetic Mechanism Development	138

Northwestern University

V.5	A Novel Lubricant Formulation Scheme for 2% Fuel Efficiency Improvement	166
-----	---	-----

Oak Ridge National Laboratory

II.3	Improving Vehicle Fuel Economy Through Increasing Fuel Octane Ratings	38
II.6	Co-Optima: Gasoline-Like Fuel Effects at High Load	50
II.8	GDI Fuel Effects on PM Emissions	61
II.9	Fuel Compatibility and Opportunities with Emissions Controls	65
III.3	Accelerate Development of ACI/LTC: ORNL Single- and Dual-Fuel ACI	90
V.10	Characterizing Impact of Engine Lubricant and Fuel Properties on LSPI	197
V.11	Compatibility of Antiwear Additives with Non-Ferrous Engine Bearing Alloys	202
V.12	Lubricant Effects on Emissions and Emissions Control Technologies	209
V.13	ORNL-GM: Development of Ionic Liquid-Additized, GF-5/6 Compatible Low-Viscosity Oils for Automotive Engine and Rear Axle Lubrication for 4% Improved Fuel Economy	213
VI.1	Gasoline Engine and Fuels Offering Reduced Fuel Consumption and Emissions (GEFORCE)	228

Pacific Northwest National Laboratory

IV.1	Fuel Property Database	122
V.14	High Efficiency Lubricant Oils and Additives Research	218
V.15	Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils	223
VI.2	Unconventional and Renewable Hydrocarbon Fuels	231

Robert Bosch, LLC

VI.9	High-Efficiency Cost-Optimized Spark-Ignited Natural Gas (HECO-SING) Engines	259
------	--	-----

Sandia National Laboratories

II.1	Alternative Fuels DISI Engine Research -- Autoignition Metrics	27
II.4	Alternative Fuels DISI Engine Research -- Stratified Lean and Homogeneous Lean	41
III.2	Autoignition Fundamentals of Fuels for Boosted SI and LTGC Engines	84
III.4	Accelerate Development of ACI/LTC: Fuel Effects on RCCI Combustion	95
III.5	Improved Mixing-Controlled Combustion Strategies and Fuels for High-Efficiency Compression Ignition Engines	100

Southwest Research Institute

VI.6	Reduced Petroleum Use Through Easily-Reformed Fuels and Dedicated Exhaust Gas Recirculation	247
------	---	-----

Stony Brook University

VI.5	Single-Fuel Reactivity Controlled Compression Ignition Combustion Enabled by Onboard Fuel Reformation	243
------	---	-----

University of Michigan

VI.4	Utilizing Alternative Fuel Ignition Properties to Improve SI and CI Engine Efficiency	237
------	---	-----

University of Tennessee

V.3	Hybrid Ionic-Nano-Additives for Engine Lubrication to Improve Fuel Efficiency	153
-----	---	-----

Valvoline

V.6	Improve Fuel Economy Through Formulation Design and Modeling	174
-----	--	-----

(This page intentionally left blank)

