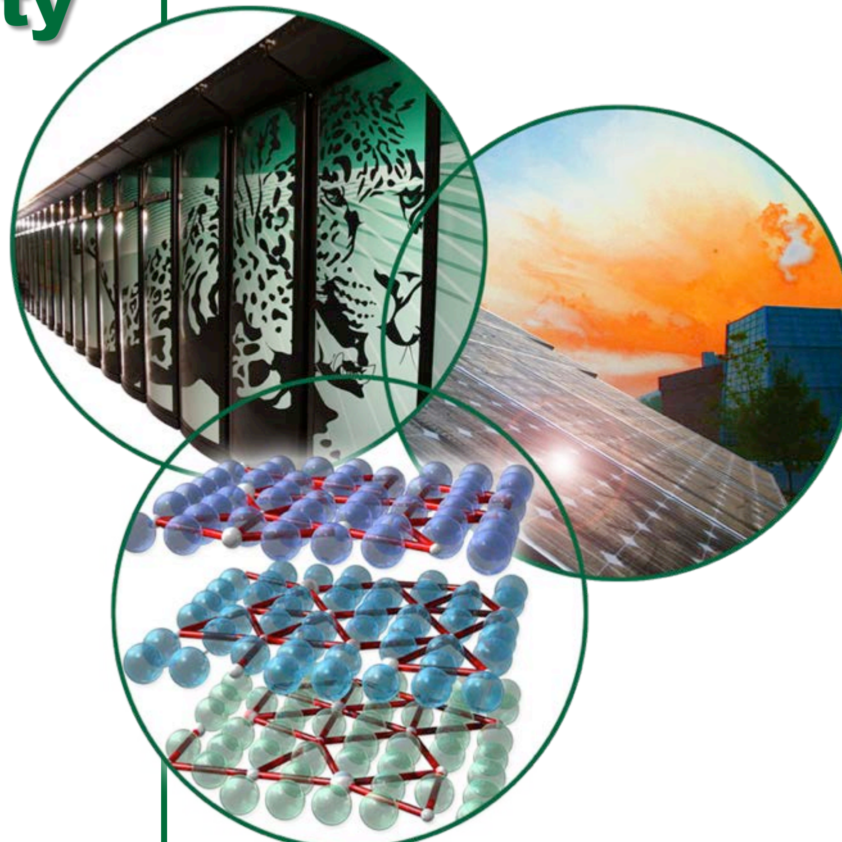
Ionic Liquids as Anti-Wear Additives for Next-Generation Low-Viscosity Fuel-Efficient Engine Lubricants

Project ID: FT014



ORNL: Jun Qu, Peter Blau (retired), Huimin Luo, Sheng Dai, Todd Toops, Brian West, and Bruce Bunting (retired)

GM: Michael Viola, Gregory Mordukhovich (left GM), and Donald Smolenski (retired)

DOE Management Team:

Steve Goguen, Kevin Stork and Steve Przesmitzki

2014 DOE Vehicle Technologies Program Annual Merit Review, June 19, 2014

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

- Project (CRADA) start date: May 28, 2009
- Project (CRADA) end date: Sept. 28, 2013
- Percent complete: 100%

Budget

- Total project funding
  - DOE share: $1.0M
  - GM in-kind cost share: $780K
- FY13 funding
  - DOE share: $100K (carryover from FY12)
  - GM in-kind cost share: $200K
- FY14 funding
  - $0 (project completed, follow-on ORNL-GM joint proposal submitted to FOA 991)

Barriers

- 10-15% energy generated in an IC engine is lost to parasitic friction, which is governed by the engine lubricant.
- Low-viscosity engine oils increase fuel economy but post challenges on wear protection.
- Emission catalysts ‘poisoned’ by conventional anti-wear additives.

Partners

- CRADA partner: General Motors
- Other collaborators: Lubrizol and Cytec Industries

Relevance

- **Objective: Investigate the potential of using ionic liquids (ILs) as lubricants and/or lubricant additives specifically for internal combustion engine applications.**
- **Potential benefits:**
  - **Improved engine fuel efficiency without wear penalty by using ionic liquid-additized low-viscosity engine oils.**
  - **Reduced exhaust emission by lower fuel consumption and less adverse effects on emission catalysts.**

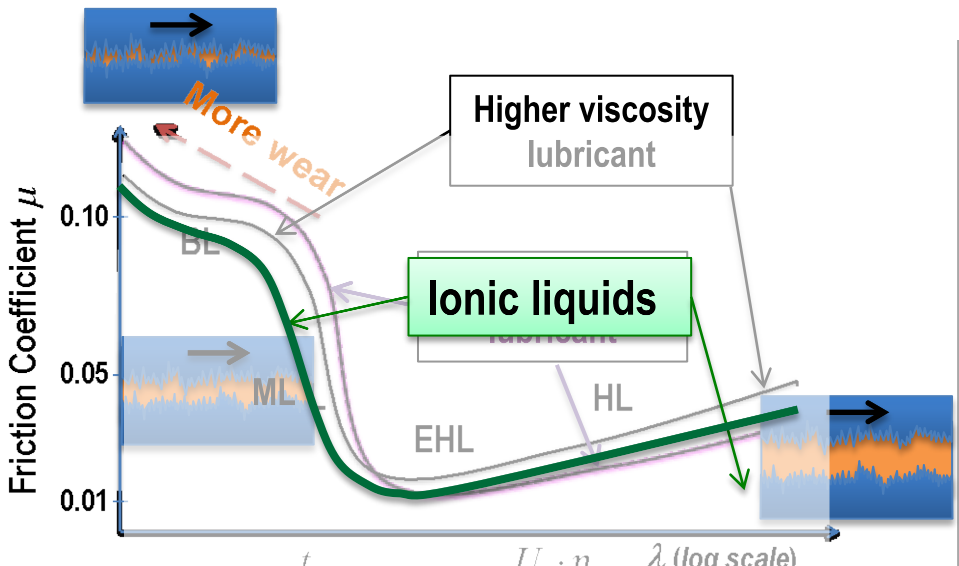
Milestones

- **Sept. 28, 2013 – Demonstrate benefits of using ionic liquids as lubricant additives on multi-cylinder engine dynamometer tests.** ***(complete)***
- **Oct. 28, 2013 – CRADA Final report to DOE VTP Office.** ***(complete)***

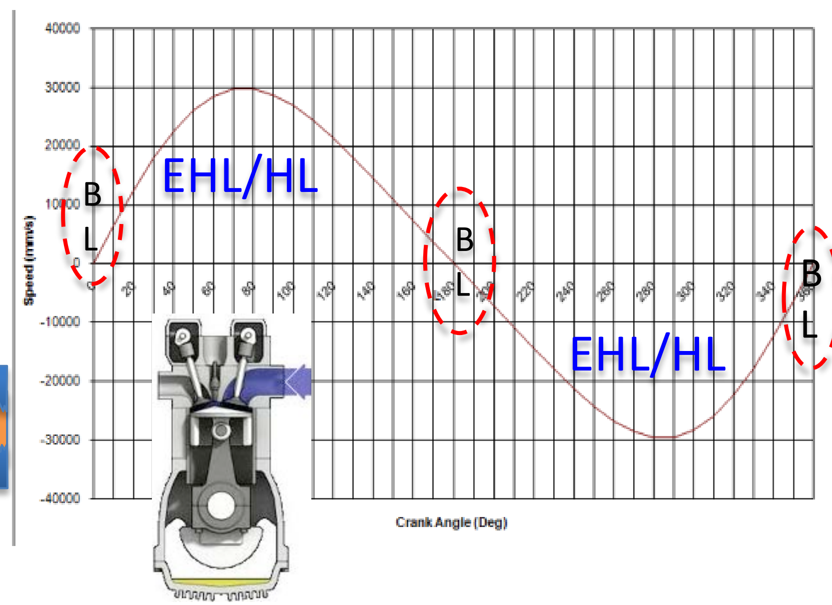
Approach

- **Engine lubrication: ~80% at HD/EHD, 10-15% at ML, and 5-10% at BL**
- **Lower oil viscosity → reduced HD/EHD drag (better fuel economy) but more surface asperity collisions (wear challenge)**

- **Approach: developing oil-soluble ionic liquids as next-generation ashless AW additives to allow the usage of lower-viscosity engine oils.**



$$\lambda = \frac{t}{\sigma}, \quad where \quad t \propto \frac{U_e \cdot \eta}{P}$$



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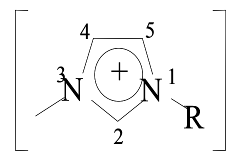
Background – Ionic liquids

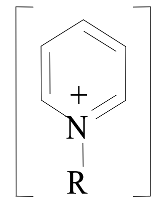
- **ILs as neat lubricants or base stocks**
  - **High thermal stability (up to 500 ºC)**
  - **High viscosity index (120-370)**
  - **Low EHL/ML friction due to low pressure-viscosity coefficient**
  - **Wear protection by tribo-film formation**
  - **Suitable for specialty bearing components**

- **ILs as oil additives**
  - **Potential multi-functions: AW/EP, FM,** *corrosion inhibitor, detergent*
  - **Ashless/low sludge**
  - **Allow the use of lower viscosity oils**
  - **Cost effective and easier to penetrate into the lubricant market**

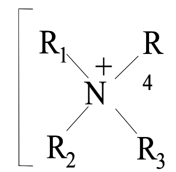
Ionic liquids are 'room temperature molten salts', composed of cations & anions, instead of neutral molecules.



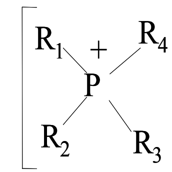
1-alkyl-3-methyl-imidazolium



N-alkyl-pyridinium



Tetraalkyl-ammonium



Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

<u>Common Cations</u>

$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[(CF_3SO_2)_2N]^-$ (Tf_2N)	$[CF_3SO_3]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[(C_2F_5SO_2)_2N]^-$ (BETI)		Br^-, Cl^-, I^-
$[BR_1R_2R_3R_4]^-$		$[Al_2Cl_7]^-$, $[AlCl_4]^-$
$[P(O)_2(OR)_2]^-$ (phosphate)		
$[P(O)_2(R)_2]^-$ (phosphinate)		

<u>Common Anions</u>

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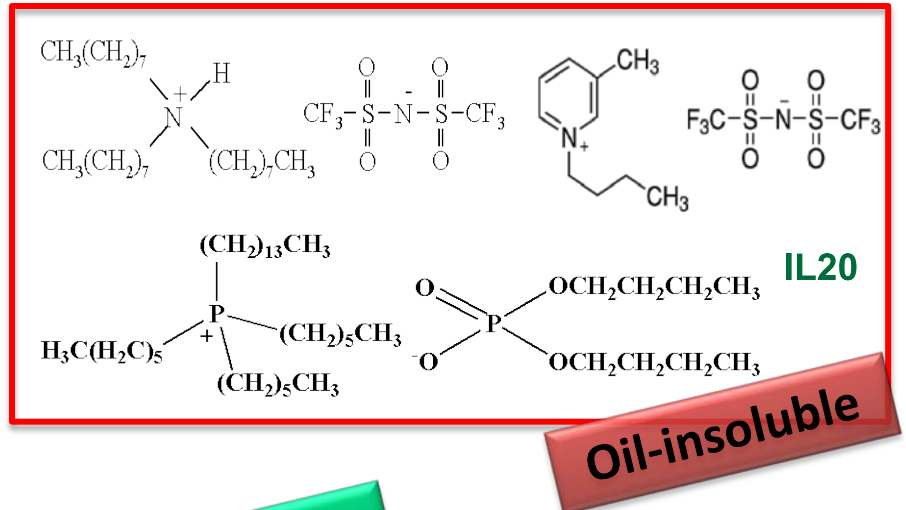
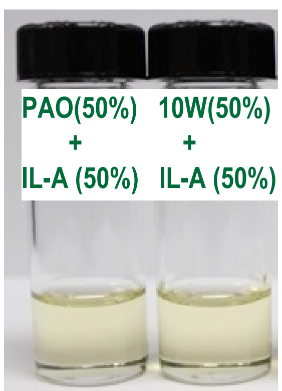
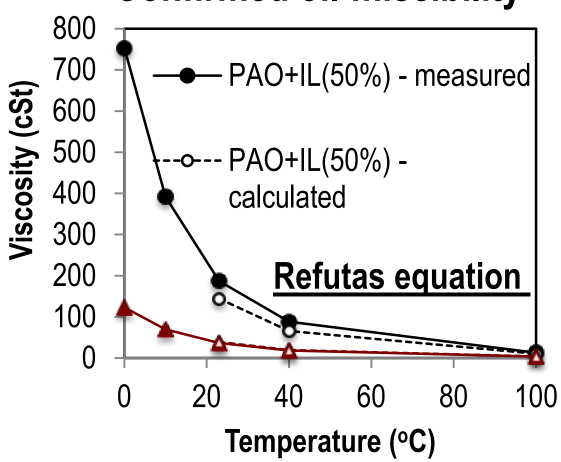
ORNL’s breakthrough in oil-miscible ionic liquids

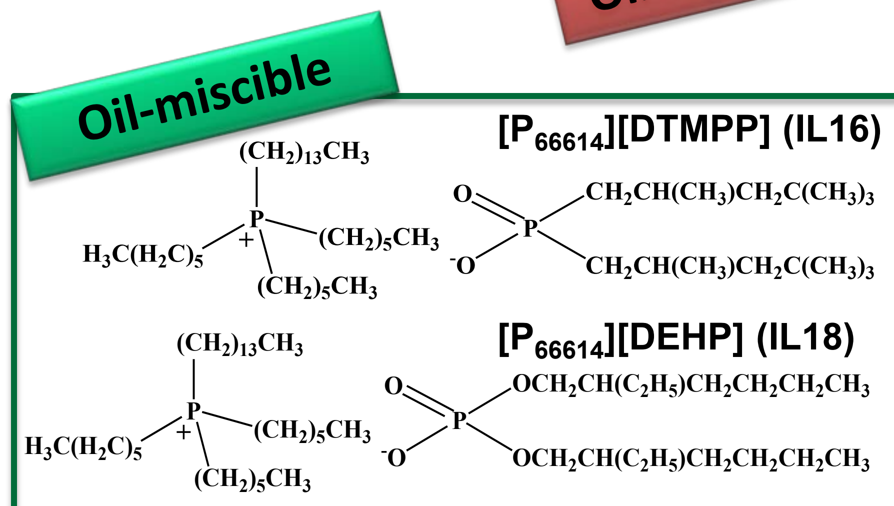
- **Most ILs have very limited oil-solubility (<<1%).**
  - 2D cations or small anions w/ intense charges
- **Molecular design criteria for oil-miscible ILs:**
  - 3D quaternary cations + surfactant anions
  - w/ long alkyls to dilute the charge to be compatible with neutral oil molecules





Confirmed oil-miscibility





B. Yu, and J. Qu, et al., Wear (2012) 289 (2012) 58.*
J. Qu, et al., ACS Applied Materials & Interfaces 4 (2) (2012) 997.

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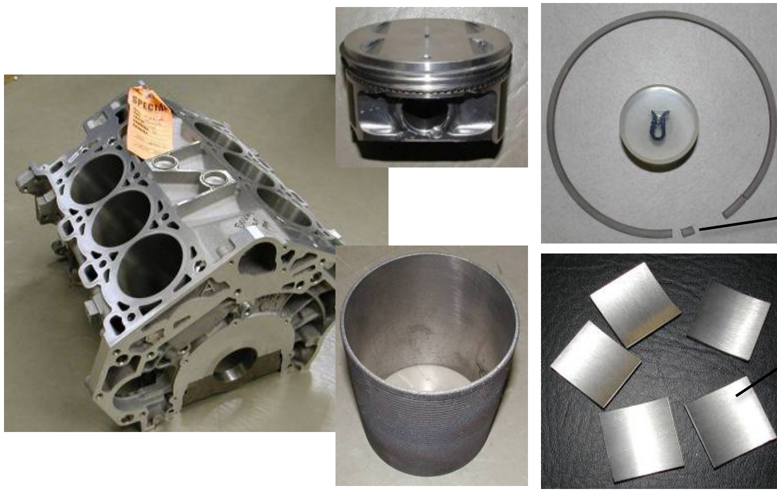
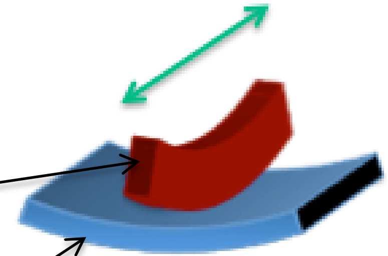
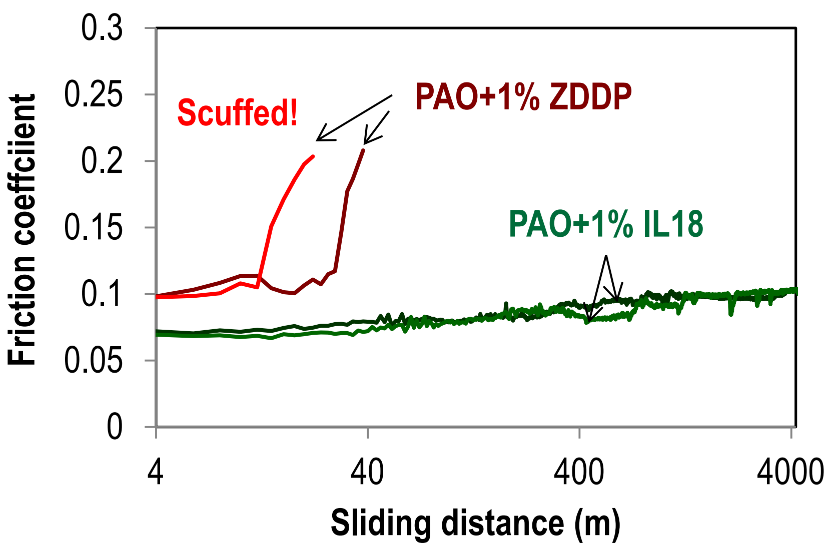
Bench test results suggested IL18 more effective in anti-scuffing than ZDDP

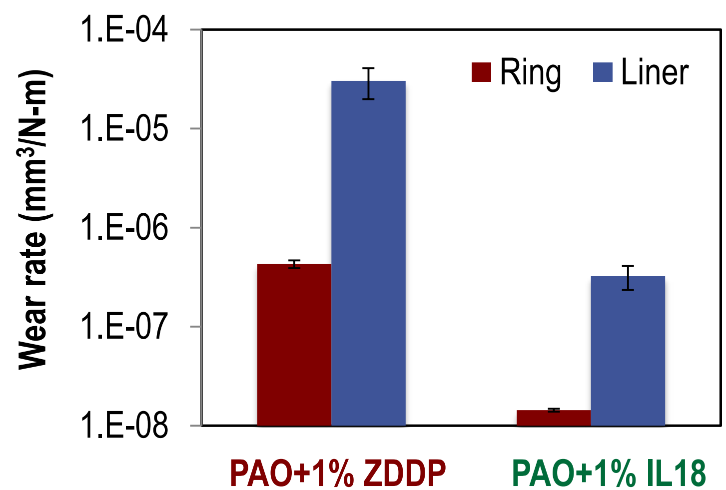




Ring-on-liner reciprocating sliding test

- Base oil: PAO 4
- IL or ZDDP treat rate: 1 wt%
- Temperature: 100 °C

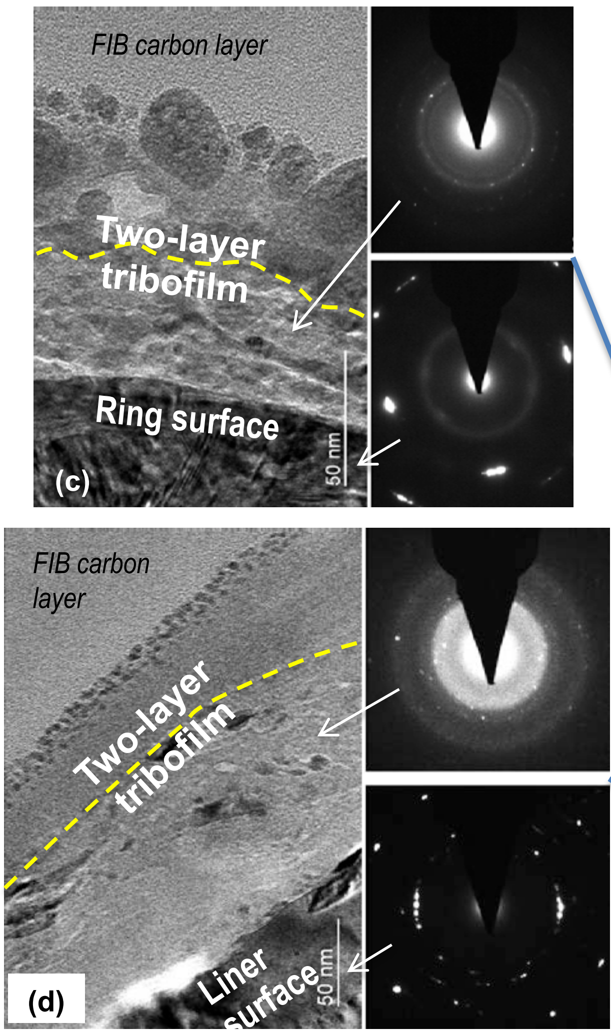




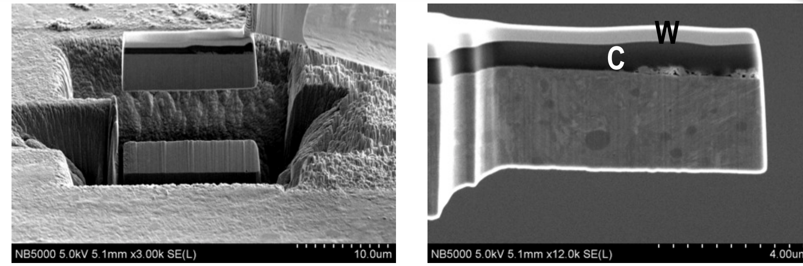
J. Qu, et al., Tribology International, 71 (2014) 88–97.

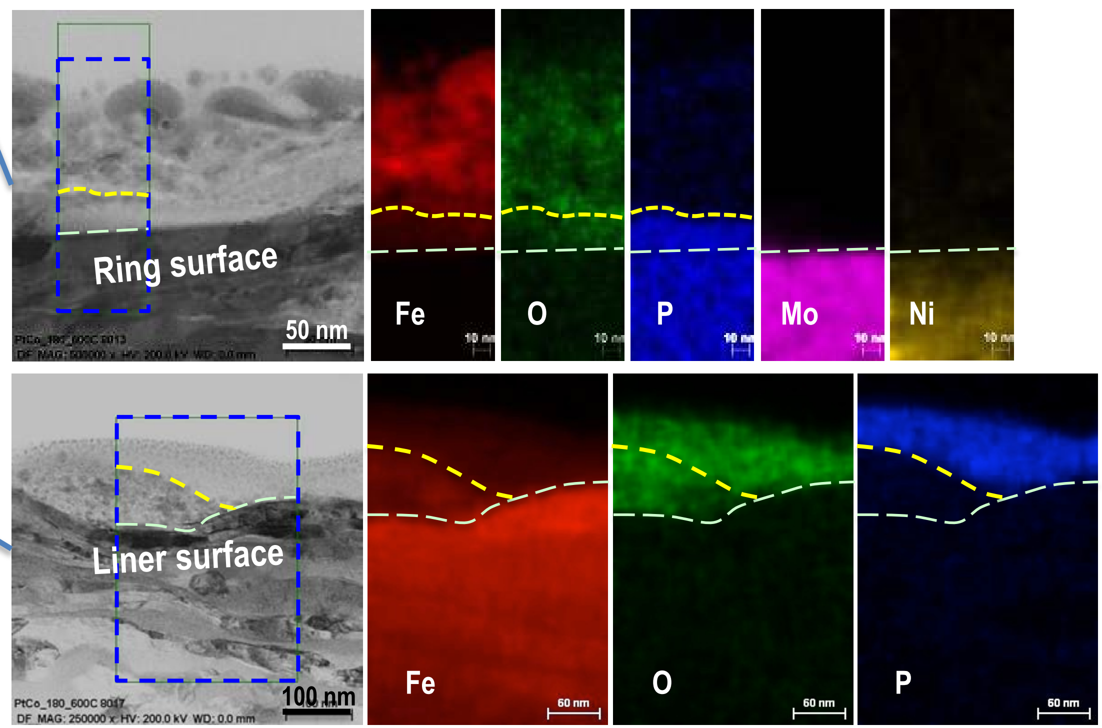
IL18 formed anti-wear tribofilms on both piston ring and cylinder liner surfaces

TEM/EDS/Electron diffraction



Focused-ion beam (FIB)





J. Qu, et al., Tribology International, 71 (2014) 88–97.

Technical accomplishments – summary

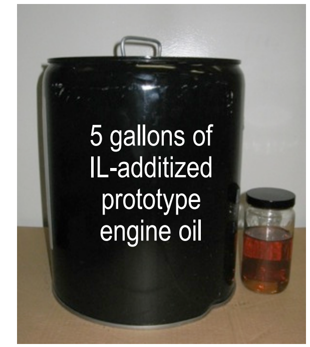
FY 2013 accomplishments:

- 1st prototype IL-additized, fully-formulated low-viscosity (similar to the proposed SAE 8) engine oil has been formulated and produced.
- Tribological bench tests of the IL-additized engine oil demonstrated 20% friction reduction in elastohydrodynamic/mixed lubrication and 38% wear reduction compared to Mobil 1 SAE 5W-30 engine oil.
- High-temperature high-load engine dynamometer tests demonstrated comparable wear protection between the IL-additized low-viscosity engine oil and Mobil 1 SAE 5W-30 engine oil.
- Sequence VID engine dynamometer tests of the prototype IL-additized engine oil demonstrated >2% improved fuel economy compared to Mobil 1 SAE 5W-30 engine oil.
- Demonstrated potentially less adverse impact on three-way catalyst (TWC) for IL18 compared to ZDDP.

Application submitted for the 2014 R&D 100 Award.

First prototype IL-additized fully-formulated low-viscosity engine oil

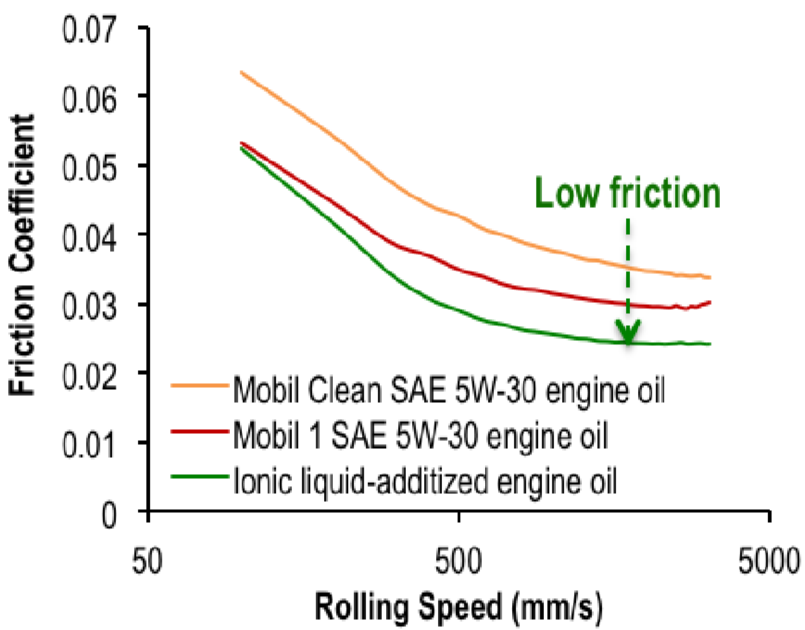
- **Prototype IL-additized fully-formulated engine oil using PAO 4 cSt as the base oil and 1.0 wt.% [P_{66614}][DEHP] (IL18) as AW has been formulated and produced by Lubrizol.**
  - **1st IL-additized fully-formulated engine oil in the literature**
- **Ultra-low viscosity (comparable to the proposed SAE 8).**

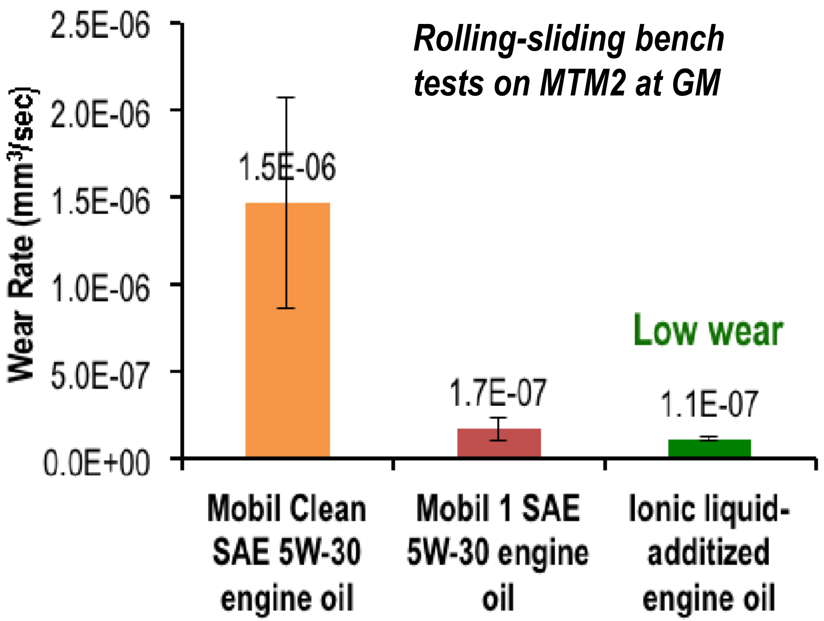


	cSt @ 40 °C	cSt @ 100 °C	HTHS (cP @150 °C)
Mobil 1™ 5W-30 engine oil	**64.27**	**11.38**	**3.11**
Mobil Clean™ 5W-30 oil	**56.1**	**10.1**	**3.06**
SAE XW-20 engine oil		>6.9, <9.3	>2.6
SAE XW-16 (newest)		>6.1, <8.2	>2.3
proposed SAE XW-12			*>2.0*
proposed SAE XW-8			*>1.7*
IL-additized prototype engine oil	**25.53**	**5.38**	**1.85**

Superior friction/wear behavior of the prototype IL-additized engine oil

- 33% friction reduction in ML/EHL and 92% wear reduction in BL compared to Mobil Clean 5W-30 engine oil.
- 20% friction reduction in ML/EHL and 38% wear reduction in BL compared to Mobil 1™ 5W-30 engine oil.





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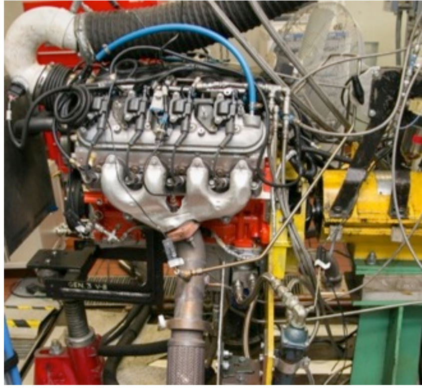
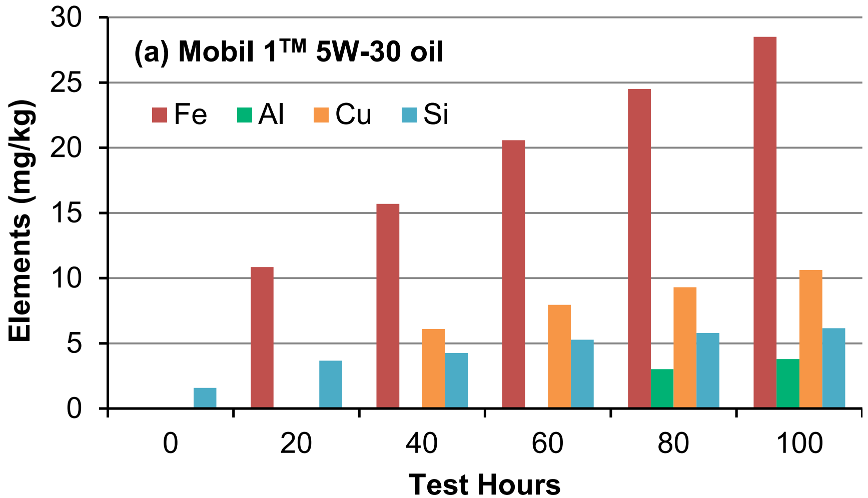
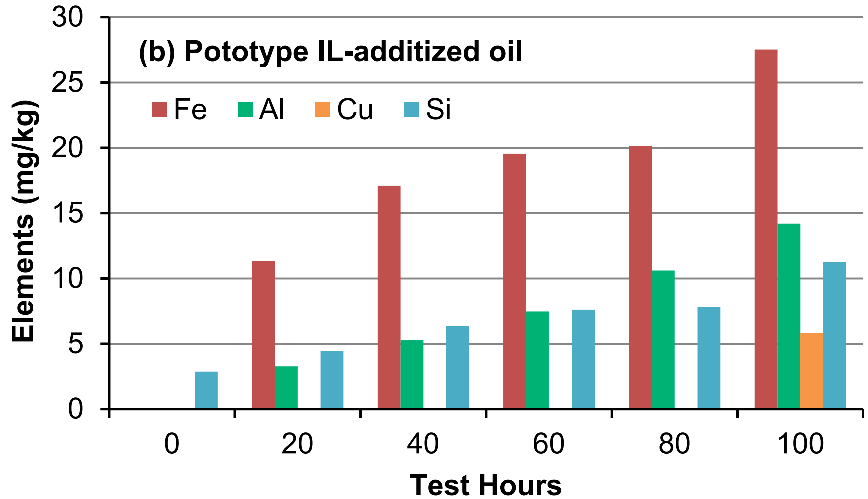
High-temperature high-load (HTHL) engine tests at GM demonstrated excellent wear protection



- HTHL engine dyno test condition
  - LSX 6.2L Gen4 small block engine, rated at 450 HP
  - 100 hrs at 2700 rpm, 120 N load, and 145 °C oil sump temp
  - Oil samples (2 oz) taken at fresh, 20, 40, 60, 80 and 100 hrs
- **Oil consumed: 41.2 oz for IL-additized oil and 41.9 oz for Mobil 1™ 5W-30**
- **HTHS viscosity after 100 hrs: 1.85→2.03 cP for IL-additized oil and 3.11→3.17 cP for 5W-30**
- **Engine wear and oil aging performance comparable to that of Mobil 1™ 5W-30**





IL provides excellent wear protection at such a low oil viscosity!

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Sequence VID engine dynamometer tests at InterTek demonstrated >2% improved fuel efficiency over Mobil 1 SAE 5W-30 engine oil

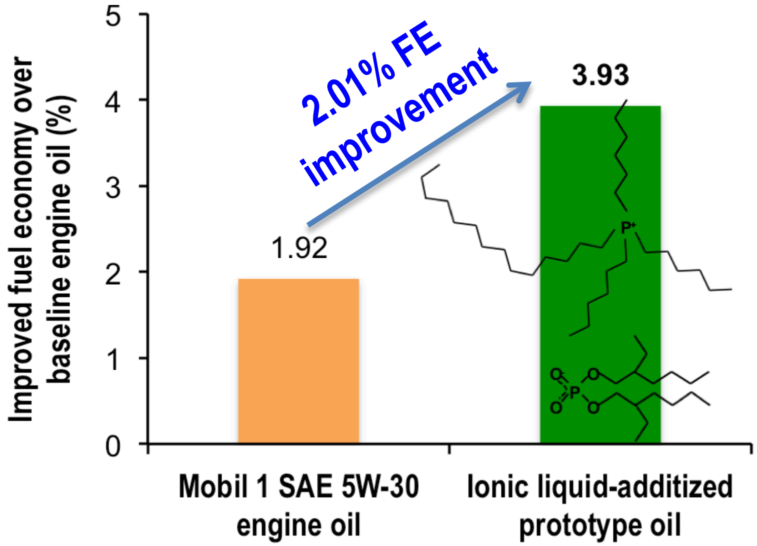
- GF-5 / Sequence VID (ASTM D 7589) test condition
  - 2008 Cadillac SRX 3.6L High Feature (HF) V6, 4-cycle engine
  - Baseline oil: SAE 20W-30 engine oil w/o FM or VII
  - A flush and run type procedure with the test oil evaluated in between two baseline runs
  - 200-2250 rpm, 20-110 N-m torque, 35-120 ^{o}C oil sump temp
  - Two aging stages: 16 hrs + 84 hrs

✧ Fuel economy 3.93% higher than the baseline SAE 20W-30 oil (w/o FM or VII)

✧ Fuel economy 2.01% higher than the Mobil 1™ SAE 5W-30 engine oil

[1] "Molten Salts Could Improve Fuel Economy," Inside Science, Nov. 15, 2013.

[2] "Oak Ridge-GM prototype low-viscosity ionic liquid-additized engine oil delivers 2% fuel economy improvement over 5W-30," Green Car Congress, Dec. 30, 2013.



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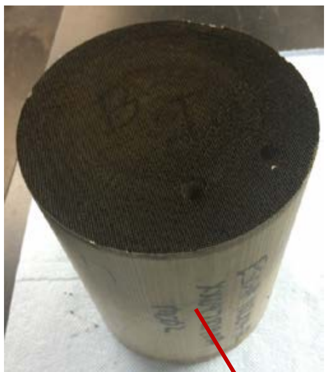
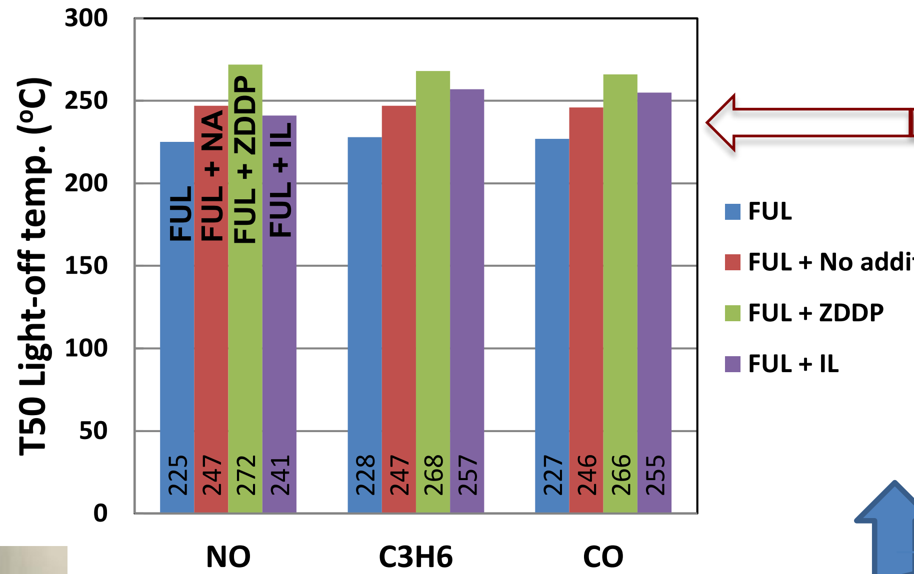
IL18 demonstrated potentially less adverse effects on TWC compared to ZDDP

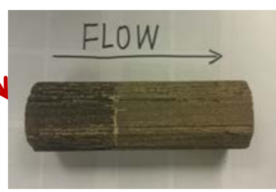
Close-coupled TWC from GM: aged to 150K miles, or the equivalent of full useful life (FUL)



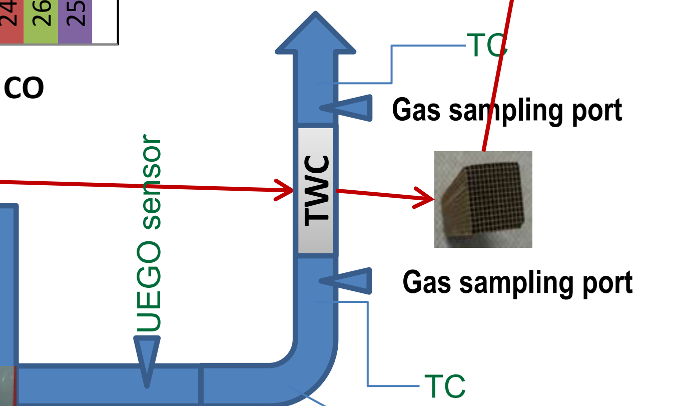


Bench reactor

Catalyst core for engine aging



Gas Genset
(3500W Briggs&Stratton)
~250cc, 3600 rpm, AFR ~12



2" pipe between engine and TWC

35 g of IL18 or ZDDP blended into the gasoline to simulate the maximum lifetime AW additive consumption in a modern automotive engine

Make-up air to get AFR = 14.6 (~50 L/min); before muffler

 Managed by UT-Battelle for the U.S. Department of Energy

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OAK RIDGE National Laboratory

Responses to Previous Year Reviewers' Comments

- **Not applicable – this project was not reviewed last year.**

Collaboration

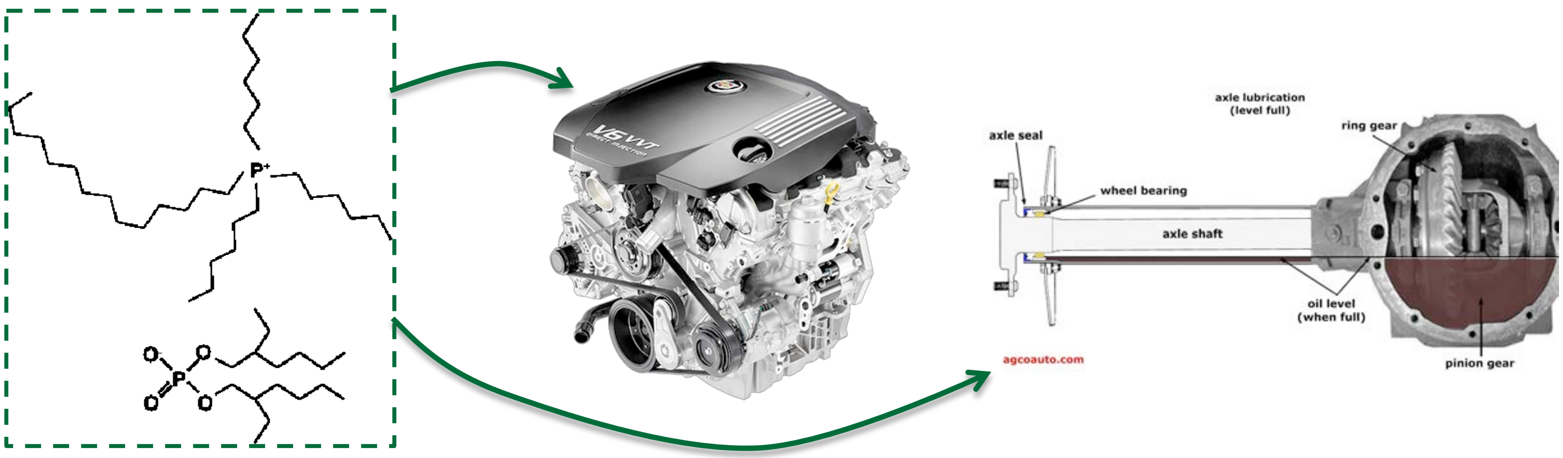
- General Motors (CRADA NFE-08-01715 partner)
  - Participated in tribological bench testing
  - Coordinated with Lubrizol for formulating the 1st ever prototype ionic liquid-additized engine oil
  - Led engine dynamometer testing (HTHL and Seq. VID)
  - Provided TWC for investigation of the IL's impact
- Lubrizol
  - Conducted standard oil additive tests on the candidate ionic liquid
  - Formulated 1st ever prototype ionic liquid-additized engine oil
- Cytec Industries
  - Supplied feed stocks to ORNL for synthesizing ionic liquids

Remaining Challenges and Barriers

- Ionic liquids' molecular structures remain to be optimized.
- Ionic liquids' lubricating mechanism is not fully understood yet.
  - Roles of cations and anions in surface absorption and tribofilm formation
  - Interactions among ionic liquid ions, base oil molecules, and contact surfaces in different lubrication regimes
- Compatibility of ionic liquids with conventional lubricants requires systematic investigation.
  - Synergistic effects between ILs and ZDDP on friction and wear reduction have been observed and offer opportunities for performance improvement and cost reduction (less IL needed).
- Ionic liquids' anti-wear effectiveness on non-ferrous bearing surfaces, such as bronze and Al-Si alloys (used for connecting rod end bushings/bearings), is little known.
- Ionic liquids' lubricating functionality for other vehicle bearing components, such as rear axle, is yet to be studied.

Proposed Future Work

- **A new ORNL-GM joint proposal was submitted to DOE in response to the VTP's DE-FOA-0000991 (Topic 11A) for follow-on R&D on**
  - **Further development of ionic liquid-additized GF-5/6 low-viscosity engine lubricants, and expansion of the ionic liquid additive technology to rear axle lubricants for a combined 4% improved fuel economy.**



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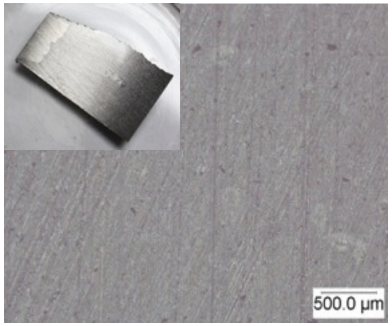
Summary

- **Relevance:** Investigate the potential of using ionic liquids (ILs) as lubricants and/or lubricant additives specifically for internal combustion engine applications.
- **Approach/Strategy:** Developing oil-soluble ionic liquids as next-generation ashless AW additives to allow the usage of lower-viscosity engine oils.
- **Accomplishments in FY 2013:**
  - 1st prototype IL-additized, fully-formulated low-viscosity engine oil has been produced.
  - Engine dynamometer tests demonstrated >2% improved fuel economy and comparable wear protection between the IL-additized low-viscosity engine oil and Mobil 1 SAE 5W-30 engine oil.
  - Demonstrated potentially less adverse impact on TWC for an IL compared to ZDDP.
- **Collaborations:**
  - CRADA partner: General Motors
  - Other collaborators: Lubrizol and Cytec Industries
- **Proposed Future Work (pending FOA proposal):**
  - Further development of ionic liquid-additized GF-5/6 low-viscosity engine lubricants and expansion of the ionic liquid additive technology to rear axle lubricants for a combined 4% FE improvement.

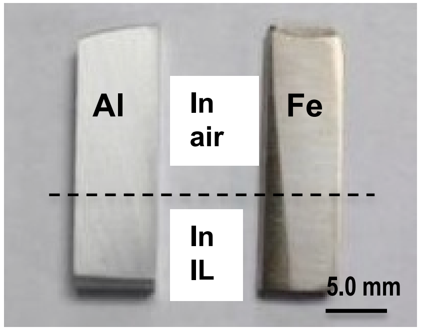
Technical Back-up Slides

ORNL's oil-miscible ILs are non-corrosive with good wettability and high thermal stability

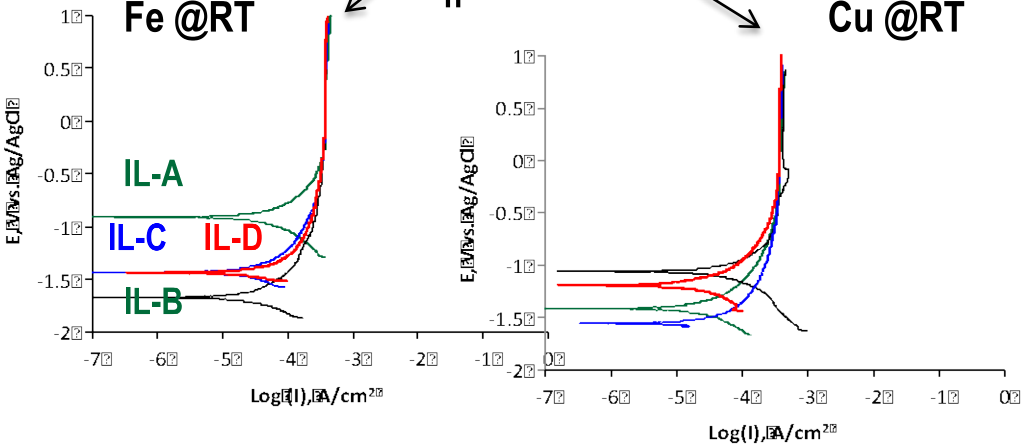
- Non-corrosive to Fe or Al



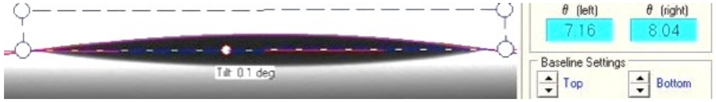
IL-A on cast iron surface in ambient for 60 days



Al and cast iron submerged in IL-A at 135 °C for 7 days



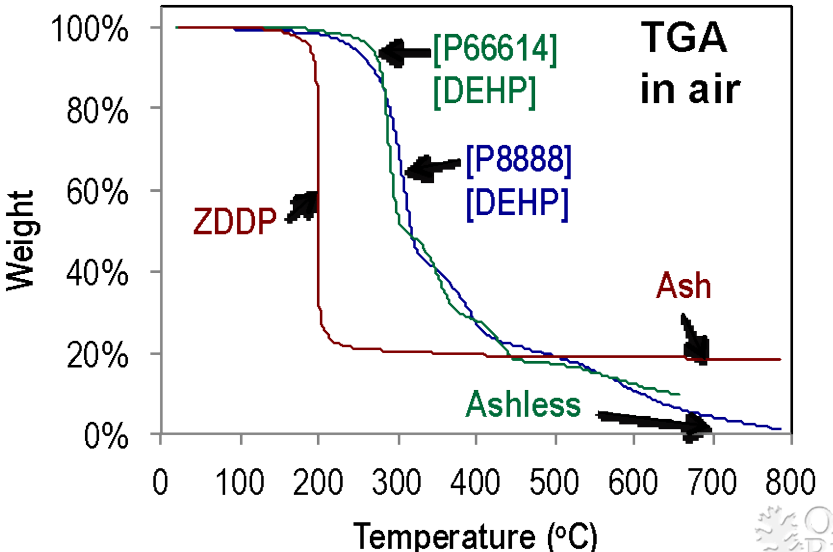
- Excellent wettability



	Contact angle on cast iron
PAO 4 cSt base oil	13.0
$[P_{66614}]$[BTMPP] (IL16, oil-miscible)	6.3
$[P_{66614}]$[DEHP] (IL18, oil-miscible)	7.6
$[BMIM][NTf_2]$ (oil-insoluble)	41.7

J. Qu, et al., ACS Applied Materials & Interfaces 4 (2) (2012) 997.

- High thermal stability and ashless



ILs' concentrations in GF-5 engine oils

3.a Catalyst Compatibility

Phosphorus Content, ASTM D4951	0.08% (mass) maximum
Phosphorus Volatility, ASTM D7320 (Sequence IIIGB, phosphorus retention)	79% minimum
Sulfur Content, ASTM D4951 or D2622	
0W-XX, 5W-XX	0.5% (mass) maximum
10W-30	0.6% (mass) maximum

3.b Wear

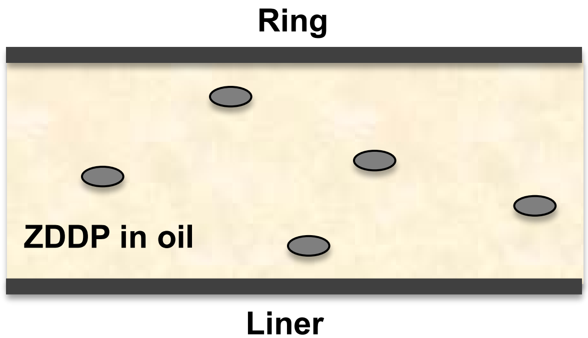
Phosphorus Content, ASTM D4951	0.06% (mass) minimum

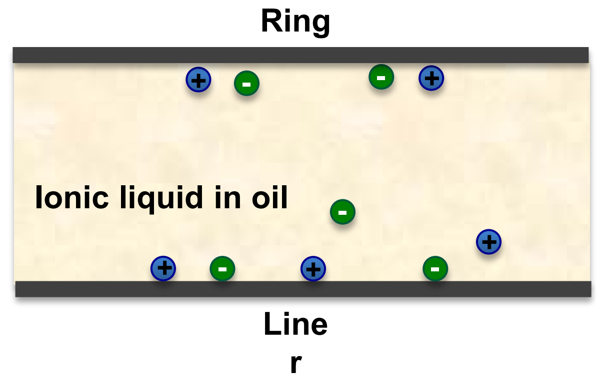
ILSAC GF-5

	MW	P (wt%)	S (wt%)	Zn (wt%)	Allowable concentration
ZDDP (Octyl)	771	8.04	16.6	8.43	**0.75 - 0.99 wt%**
$[P_{66614}]$[DEHP] (IL18)	804	7.71	0	0	**0.78 - 1.04 wt%**
$[P_{66614}]$[BTMPP] (IL16)	772	8.03	0	0	**0.75 - 0.99 wt%**

Why IL performed better than ZDDP in anti-scuffing? – *a hypothesis*

- **Before contact and rubbing…compared neutral ZDDP molecules, ionic liquids tend to absorb to the metal surface to possibly provide a higher localized concentration at the contact interface…**





- **In contact and rubbing…ionic liquids react with wear debris and metal surface to form an anti-wear tribofilm…**

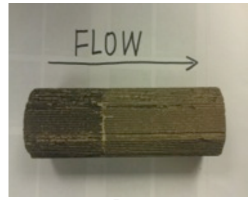
This presentation does not contain any proprietary, confidential, or otherwise restricted information

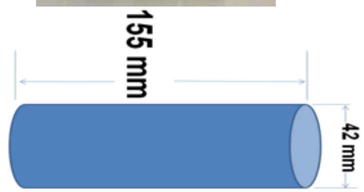
IL-18 compatibility with TWCs evaluated

FUL-TWC

Close-coupled TWC from GM: aged to full useful life (FUL) equivalent (150K miles) using accelerated techniques

Catalyst core for engine aging

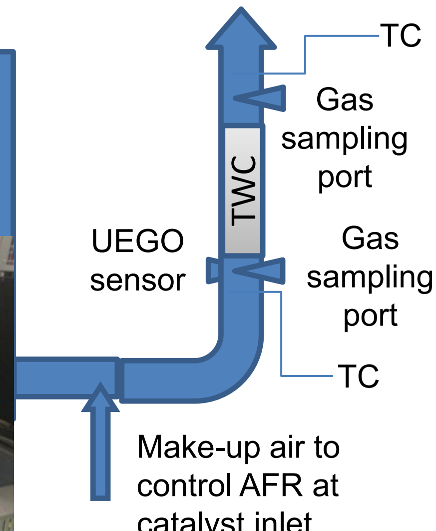




Loaded into exhaust can, ready for aging using a gasoline genset

- **Lubricant additives included in the fuel**
- **Amount (35 g) based on average lifetime oil consumption**
- **Three runs**
  - **IL-18**
  - **ZDDP**
  - **No Additive (NA)**

Gas Genset
3500W Briggs&Stratton
~250cc, 3600 rpm, AFR ~12

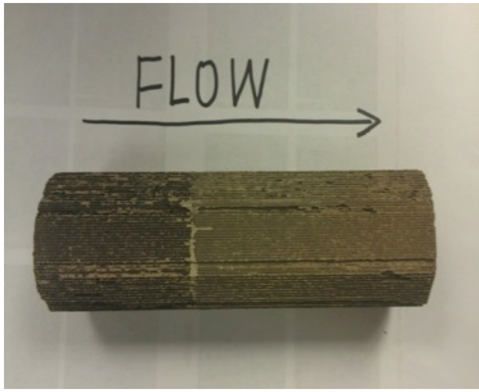


Engine aging:

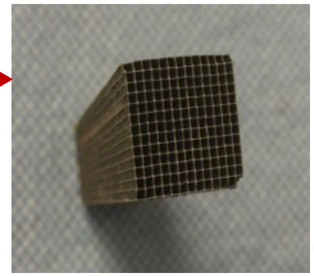
1. **Switch between rich and lean to avoid high catalyst temperatures**
2. **8 gallons gasoline consumed within 25 hours**
3. **T_{inlet} < 900C**

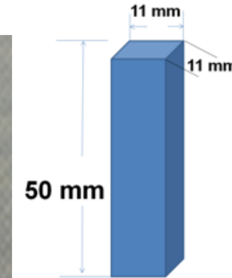
Aged catalysts evaluated using flow bench reactors

Aged catalyst core

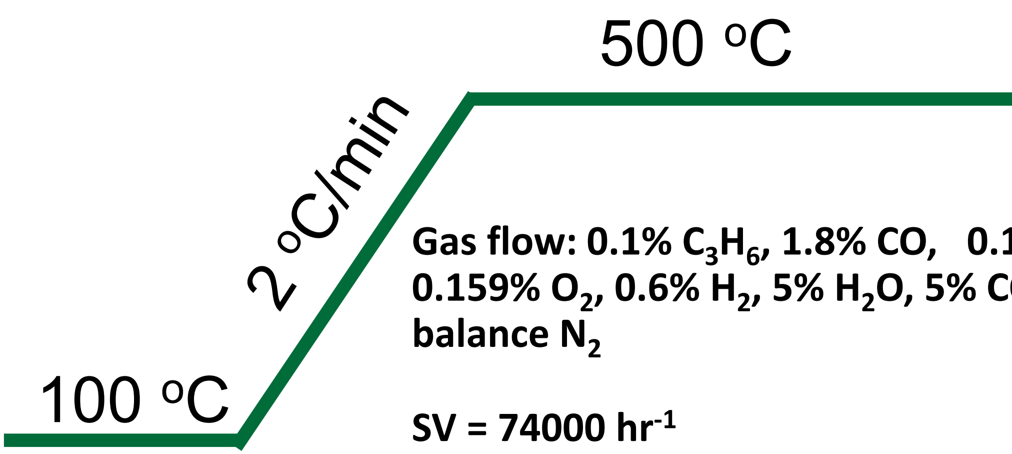


Small aged catalyst core





Catalyst loaded into quartz tube reactor



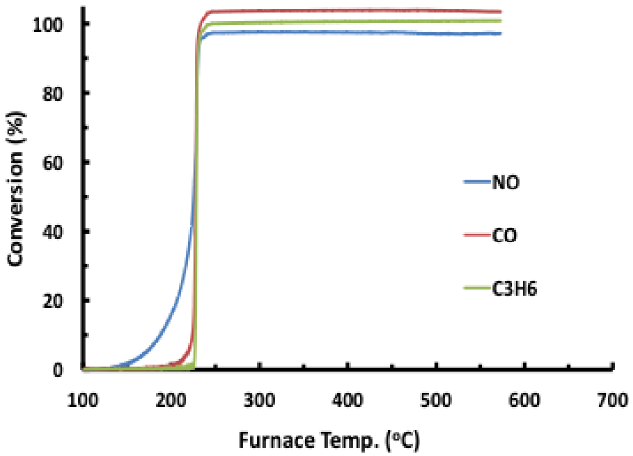
Gas flow: 0.1% C_3H_6, 1.8% CO, 0.12% NO, 0.159% O_2, 0.6% H_2, 5% H_2O, 5% CO, and balance N_2

SV = 74000 hr^{-1}

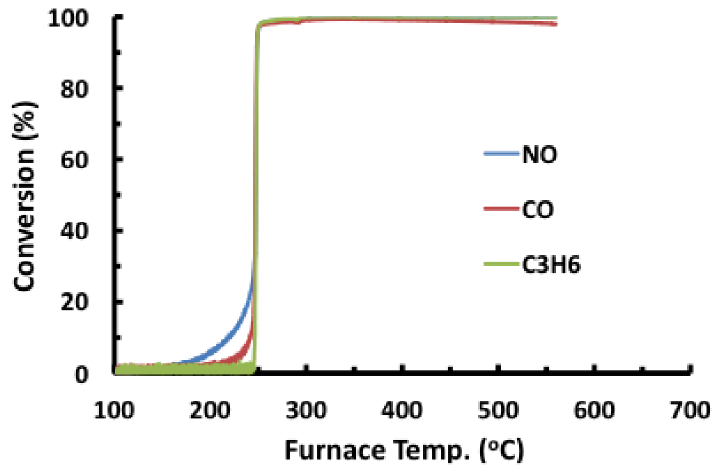
bench reactor

TWC inlet evaluated to measure impact of additives

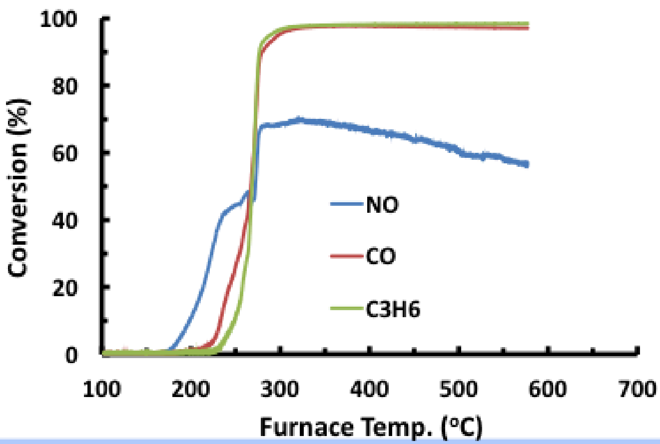
FUL



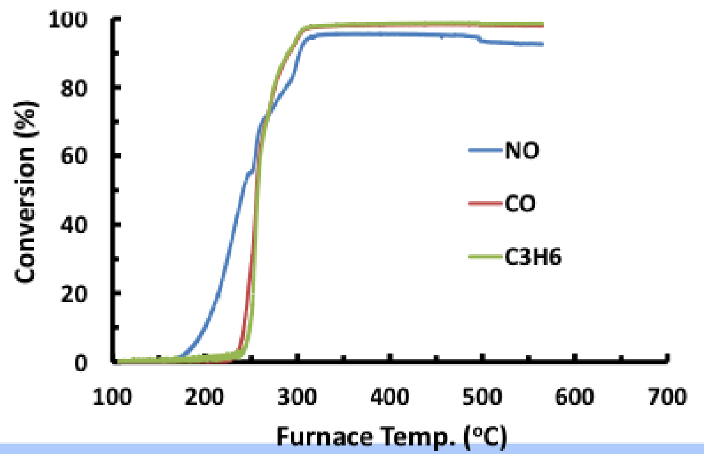
FUL + No additive (NA)



FUL + ZDDP



FUL + IL



- **Difference between FUL+NA and FUL is minor for all 3 gases**
- **ZDDP-aged TWC shows the highest deactivation**
- **IL18 shows less impact than ZDDP**