Ionic Liquids as Multi-Functional Lubricant Additives to Enhance Engine Efficiency
– An award of FOA0000239

Project ID: FT014

ORNL: Jun Qu, Peter Blau, Huimin Luo, Sheng Dai, Brian West
Shell: Brian Papke, Cheng Chen, Hong Gao

DOE Management Team: Kevin Stork and Steve Przesmitzki

2013 DOE Vehicle Technologies Program Annual Merit Review, May 16th 2013
Overview

Timeline
- Project (CRADA) start date: July 23, 2012
- Project (CRADA) end date: July 22, 2015
- Percent complete: 20%

Budget
- Total project funding $1.6M
  - DOE share: $1.2M
  - Shell in-kind cost share: $400K
- FY12 funding
  - DOE share: $400K
  - Shell in-kind cost share: $100K
- FY13 funding
  - DOE share: $400K (expected)
  - Shell in-kind cost share: $150K

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

Partners
- Project lead: ORNL
- CRADA partner: Shell Global Solutions (U.S.)
Relevance – Objectives

• **Objective:** Develop and demonstrate oil-soluble ionic liquids as engine oil additives to substantially improve the mechanical efficiency of internal combustion engines.
  – Potential advantages and disadvantages of this new category of additives will be explored with a combination of systematic laboratory experiments, modeling, engine dynamometer tests, and field tests.

• **Potential benefits:**
  – The goal of this project is 2% increase on the engine fuel efficiency that would save ~80 million barrels of oil for U.S. each year.
  – Potentially produce no or less emission catalyst-poisoning compounds compared with ZDDP that would improve the catalyst life and performance to reduce emissions.
**Background – Ionic liquids**

- **ILs as neat lubricants or base stocks**
  - High thermal stability (up to 500 °C)
  - 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**
  - 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.

Common Cations

- \([PF_6]^–\)
- \([BF_4]^–\)
- \([CF_3SO_3]^–\)
- \([CF_3CO_2]^–\)
- \([NO_3]^–\)
- \([CH_3CO_2]^–\)
- \([BF_4]^–\)
- \([CF_3CO_2]^–\)
- \([NO_3]^–\)

Common Anions

- \([CF_3SO_3]^–\)
- \([CF_3CO_2]^–\)
- \([NO_3]^–\)
- \([BF_4]^–\)
- \([CH_3CO_2]^–\)
- \([CF_3CO_2]^–\)
- \([NO_3]^–\)
- \([BF_4]^–\)
- \([CH_3CO_2]^–\)
- \([CF_3CO_2]^–\)
- \([NO_3]^–\)
Background – Breakthrough in developing oil-miscible ionic liquids

- Most ILs have very limited oil-solubility (<<1%).
- [P_{66614}][DTMPP] (IL16) & [P_{66614}][DEHP] (IL18) are fully miscible with hydrocarbon oils.
  - Hypothesis: 3D quaternary ion structures w/ long hydrocarbon chains (high steric hindrance) to dilute the charge, and
  - Containing oxygen (but why?)

Background – One oil-miscible IL has demonstrated anti-wear in RT bench tests

- Adding 1-5% of ILs into PAO eliminating scuffing and reducing wear.
- Low-viscosity oil-IL single blend performing as well as the Mobil 1™ 5W30 engine oil.
- Synergistic anti-wear effect with ZDDP.


<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Viscosity (cSt, 23 °C)</th>
<th>Wear rate (x10^{-7} mm^3/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO base oil</td>
<td>34.5</td>
<td>5910 4700</td>
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<tr>
<td>PAO+IL(1-5%)</td>
<td>34.9-36.6</td>
<td>4.0-5.7 0.1</td>
</tr>
<tr>
<td>5W30 engine oil</td>
<td>141</td>
<td>4.8 0.3</td>
</tr>
<tr>
<td>5W30+IL(5%)</td>
<td>150</td>
<td>1.2 0.2</td>
</tr>
</tbody>
</table>
Approach – Developing ionic liquids-based multi-functional additives

- Majority of the stroke under EHL/HL (lower viscosity oil → lower friction) while top ring reversal region under BL (lower viscosity oil → higher wear).

- Ionic liquids (ILs) as multi-functional oil additives
  - Anti-wear tribo-film to allow the usage of lower viscosity engine oils to improve fuel economy, and
  - Smoother, low-friction tribo-film to reduce BL/ML traction.
Milestones

• July 2013 – Design and synthesize a series of oil-soluble ILs with various molecular structures and conduct standard lubricant additive evaluations. (in progress)

• July 2013 (Go/No-Go point #1) – Demonstrate 10% or more friction reduction without sacrificing the wear performance for low-viscosity oils by using the IL additives from the tribological bench tests. (in progress)
## Approach – Tasks

- **Overall program timeline: 7/23/2012 – 7/22/2015**

<table>
<thead>
<tr>
<th>Month</th>
<th>PY 1</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
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<td>Task 4. Tribological bench tests and analyses</td>
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<td>Task 7. Instrumented single-cylinder fired engine tests with emission analysis</td>
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<td>Task 8. Multi-cylinder fired engine fuel efficiency dynamometer tests (ASTM D 7589 Sequence VI)</td>
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<td>Task 9. Initial field tests</td>
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</table>
Technical accomplishments – summary

• Task 1. Design, synthesis, and optimization of oil-soluble ionic liquids
  ✓ Several groups of ILs with 3D quaternary structures designed/synthesized.

• Task 2. Characterization of physical/chemical properties of ILs
  ✓ Oil-solubility, density, viscosity, thermal stability, and corrosivity conducted on selected ILs.

• Task 3. Standard additive evaluation for ILs and lubricant formulation
  ✓ 3-month storage stability tests completed on selected ILs
  - Elastomer compatibility tests planned.

• Task 4. Tribological bench tests and analyses
  ✓ Base oil and baseline lubricants determined and acquired.
    • Shell GTL 4 cSt base oil and GTL-based formulated engine oils: fully-formulated, w/o AW, and w/o FM
  ✓ Bench tests selected: ball-on-flat sliding (BL, 100 °C) and rolling-sliding (Strubeck, 120 °C)
  ✓ Test specimens have been designed, machined, and shared between ORNL and Shell.
  ✓ Test parameters and test matrices defined.
    - Friction and wear tests being conducted.

• Task 5. Investigation and modeling lubrication mechanism of IL additives
  ✓ Contact mechanics and lubrication modeling conducted.
    - Wear mode examination and tribo-film characterization in progress.
Design and synthesis of oil-soluble ILs

- Several groups of ILs with 3D quaternary structures designed and synthesized.
  - 12 ILs fully miscible (>10%) and another 3 soluble (>1%) in Shell GTL 4 cSt base oil
  - 5 ILs fully miscible (>10%) and another 2 soluble (>1%) in Shell GTL 4-based formulated engine oil without precipitates or color change (no reaction w/ existing additives)

<table>
<thead>
<tr>
<th>Oil-solubility</th>
<th>Shell GTL 4</th>
<th>Shell GTL 4-based fully formulated engine oil</th>
<th>Shell GTL 4-based formulated oil w/o AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL-A</td>
<td>&gt;10%</td>
<td>&gt;10% (no color change)</td>
<td>&gt;10% (no color change)</td>
</tr>
<tr>
<td>IL-B</td>
<td>&gt;10%</td>
<td>&gt;10% (no color change)</td>
<td>&gt;10% (no color change)</td>
</tr>
<tr>
<td>IL-C</td>
<td>&gt;10%</td>
<td>&gt;10% (no color change)</td>
<td>&gt;10% (no color change)</td>
</tr>
<tr>
<td>IL-D</td>
<td>&gt;10%</td>
<td>&gt;10% (no color change)</td>
<td>&gt;10% (no color change)</td>
</tr>
</tbody>
</table>
Corrosion tests

Pitting test on CL35 grey cast iron at RT

Day 1

IL-C
IL-B
IL-D

Day 14

IL-A
IL-E
ZDDP

Potential dynamic polarization curve of cast iron in IL-A

Passivation

HT (135 °C) exposure for 7 days

Al6061
Cast iron

5.0 mm

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Storage and thermal stabilities

- IL-A and IL-B have passed the 3-month Shell storage stability tests at 0 °C, RT, and 25 °C.
  - No color change and no precipitates
- TGA tests revealed ashless and higher thermal stability and anti-oxidation of ILs compared to ZDDP.
- No premature thermal degradation when adding ILs into the formulated engine oil.
### ILSAC GF-5

#### 3.a Catalyst Compatibility

<table>
<thead>
<tr>
<th>Test</th>
<th>Minimum Requirement</th>
<th>Allowable Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus Content, ASTM D4951</td>
<td>0.08% (mass) maximum</td>
<td>0.75 - 0.99 wt%</td>
</tr>
<tr>
<td>Phosphorus Volatility, ASTM D7320</td>
<td>79% minimum</td>
<td></td>
</tr>
<tr>
<td>Sulfur Content, ASTM D4951 or D2622 0W-XX, 5W-XX, 10W-30</td>
<td>0.5% (mass) maximum</td>
<td>0.78 - 1.03 wt%</td>
</tr>
<tr>
<td></td>
<td>0.6% (mass) maximum</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.b Wear

<table>
<thead>
<tr>
<th>Test</th>
<th>Minimum Requirement</th>
<th>Allowable Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus Content, ASTM D4951</td>
<td>0.06% (mass) minimum</td>
<td>1.31 - 1.74 wt%</td>
</tr>
</tbody>
</table>

**Table: Molecular weight and concentration**

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>P (wt%)</th>
<th>S (wt%)</th>
<th>Zn (wt%)</th>
<th>Allowable concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZDDP (Octyl)</td>
<td>771</td>
<td>8.04</td>
<td>16.6</td>
<td>8.43</td>
</tr>
<tr>
<td>IL-A</td>
<td>804</td>
<td>7.71</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>IL-B</td>
<td>772</td>
<td>8.03</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>IL-C</td>
<td>804</td>
<td>7.71</td>
<td>0</td>
<td>0</td>
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<tr>
<td>IL-D</td>
<td>675</td>
<td>4.59</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Little change in oil viscosity by IL additives at these concentrations.
Tribological bench tests

• Ball-on-disc rolling-sliding test for Striebeck curves (BL-ML-EHL)
  – PCS Mini-Traction Machine (MTM2)
  – Ball: AISI E52100 steel (19 mm dia)
  – Disk: AISI E52100 steel
  – Temperature: 100, 120 °C
  – Load: 30 N
  – Rolling speed: 0.01-3 m/s (50% slip)

• Ball-on-flat reciprocating sliding test for boundary lubrication friction and wear
  – Plint TE-77 and TE-90 machines
  – Ball: AISI E52100 steel (10 mm dia)
  – Flat: CL35 grey cast iron (1”x1”x1/8”)
  – Temperature: 100 °C
  – Load: 50 or 100 N and speed: 0.2 m/s (ave)
  – Sliding distance: 1000 m

<table>
<thead>
<tr>
<th></th>
<th>As-is</th>
<th>+IL</th>
<th>+IL+ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTL 4 cSt</td>
<td></td>
<td></td>
<td>*Additive concentration: 0.8-1.8 wt% (to approach the max allowable phosphor content 0.08 wt%)</td>
</tr>
<tr>
<td>GTL 4+ full additive package w/o AW</td>
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<tr>
<td>GTL 4+ full additive package</td>
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</table>
IL additives reduce friction in mixed lubrication (rolling-sliding tests at Shell)

- Full Stribeck scan: 25-35% friction reductions in mixed lubrication when IL-A, IL-B, or IL-C replacing ZDDP in the engine oil.
- Sectioned Stribeck scan: 40-50% friction reductions in mixed lubrication when IL-A, IL-B, or IL-C replacing ZDDP in the engine oil.

Striebeck Scan (ave. of last 3 of 20 scans)

![Graph showing friction coefficient vs. speed]
IL additives reduce friction and wear in boundary lubrication (reciprocating sliding tests)

- IL-A: reductions of 17% in friction and 83% in wear.
- IL-C: reductions of 16% in friction and 90% in wear.
Collaboration

- **3-year CRADA (NFE-12-03876)** between ORNL and Shell Global Solutions

### RASIC Roles & Recommendations

(LEGEND: R = Responsible, S = Support, C = Consult)

<table>
<thead>
<tr>
<th>WHAT</th>
<th>R</th>
<th>S</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>Task 1. Design, synthesis, and optimization of oil-soluble ILs</td>
<td>ORNL</td>
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<td>Shell</td>
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<td><em>Vendor</em></td>
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<td>ORNL</td>
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<tr>
<td>Task 9. Initial field tests</td>
<td>Shell</td>
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<td>ORNL</td>
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</tbody>
</table>

*Through a subcontract to a commercial vendor.*
Future work

April 2013 – March 2014

• Tailor the molecular structures of ILs to optimize the physical/chemical properties and lubricating performance.

• Complete tribological bench tests and analyses of single base oil-IL blends and simple ZDDP-replacement IL-additized engine oils.

• Carry out standard additive evaluations for candidate ILs.

• Achieve initial engine lubricant formulation using top-performing IL additives.

• Conduct systematic tribological bench tests and analyses.

• Investigate and model the lubrication mechanisms of IL additives.

• Initiate single-cylinder fired engine tests for durability and emission analysis.
Summary

- Program management
  - Three-year CRADA signed between ORNL and Shell Global Solutions on July 23, 2012.
  - Project kick-off meeting at ORNL on Aug. 6-7, 2012
  - First quarterly face-to-face meeting at Shell on Nov. 13, 2013.
  - Progress teleconferences in each month.

- Technical progress
  - Several groups of ILs with 3D quaternary structures designed/synthesized.
  - Four oil-miscible, non-corrosive ILs selected for systematic evaluations, and storage stability and thermal decomposition/oxidation tests conducted.
  - Ranges of ILs’ concentrations in GF-5 engine oils determined, and oil-IL blends with maximum allowable IL contents prepared and characterized.
  - Tribological bench tests designed and test matrix defined.
  - Initial results of rolling-sliding tests showed 25-50% friction reduction in mixed lubrication when using ILs as a replacement of ZDDP in a formulated oil.
  - Initial results of reciprocating sliding tests showed >15% friction reduction and >80% wear reductions in boundary lubrication when adding ILs into a GTL base oil.
Technical Back-up Slides
**Viscosity**

- Little change in viscosity caused by IL additives.

<table>
<thead>
<tr>
<th>Viscosity (cSt)</th>
<th>23 °C</th>
<th>40 °C</th>
<th>100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell GTL 4</td>
<td>36.6</td>
<td>18.5</td>
<td>4.01</td>
</tr>
<tr>
<td>Shell GTL 4 + 1.03% IL-A</td>
<td>36.8</td>
<td>18.4</td>
<td>3.98</td>
</tr>
<tr>
<td>Shell GTL 4 + 1.03% IL-C</td>
<td>36.7</td>
<td>18.5</td>
<td>3.99</td>
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<tr>
<td>Shell GTL 4 + 0.99% IL-B</td>
<td>36.6</td>
<td>18.5</td>
<td>3.97</td>
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<tr>
<td>Shell GTL 4 + 1.74% IL-D</td>
<td>36.6</td>
<td>18.4</td>
<td>3.95</td>
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<tr>
<td>Shell GTL 4-based engine oil</td>
<td>93.4</td>
<td>42.0</td>
<td>7.99</td>
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<tr>
<td>Shell GTL 4-based engine oil w/o AW</td>
<td>94.8</td>
<td>42.8</td>
<td>8.12</td>
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<tr>
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<td>94.5</td>
<td>42.6</td>
<td>8.04</td>
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<tr>
<td>Shell GTL 4-based engine oil w/o AW +1.03% IL-C</td>
<td>95.9</td>
<td>43.2</td>
<td>8.10</td>
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<td>93.8</td>
<td>42.9</td>
<td>8.05</td>
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