Engine Friction Reduction - Part II
(Base fluid and additive technologies)

Argonne National Laboratory
2015 Annual Merit Review
June 9, 2015

Project ID # ft029

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Overview

Timeline
- Project start date: FY 13
- Project end date: FY 19
- Percent complete: 40%

Barriers
- Fuel economy improvement via lubricants and tribology
- Reduction of greenhouse gas (GHG) emissions
- Reliability/durability
  - Impact of lubes on after-treatment devices
  - Lube compatibility with alternative fuels
  - Lubricating alternative (non-traditional) materials
  - Alternative lube stocks (bio-based)

Budget
- FY 14 Project Funding: $1838K
  - DOE Share: $1588K
  - Contractor Share*: $250K
- FY 15: $970K

* CRADA in-kind and funds-in contributions

Partners
- MIT – Lube Consortium
- Vehicle and Engine OEMs
- Component OEMs
- Lubricant Suppliers
- Additive Suppliers
- Small Businesses, Academia
Tasks Objective and Relevance

**Objective:** Develop base oil and additive technologies to reduce friction in all lubrication regimes without compromising reliability and durability.

**Relevance:** Various lubricated engine components and systems operate in different lubrication regimes. Sustainable engine friction reduction to enable increased efficiency in all lubrication regimes.

- Hydrodynamic regime friction dependent largely on base oil viscosity.
- Mixed and boundary regime friction governed by additives.
- Lubricant technology is the only viable drop-in approach for legacy vehicles
- Advanced base oil may enable use of less additives.
Project Focus and Expected Outcome

- Engine lubricants consist of base oil and tribology performance functional additives.
  - Reducing the viscosity of base oil, will result in fluid film lubrication friction reduction.
  - Anti-wear, friction modifier and extreme pressure additives will reduce friction and protect surfaces under boundary regime.

- The project will focus on the development of ultra-low viscosity base oil to reduce fluid film lubrication friction under hydrodynamic and EHD regimes.

- The additives component of the project will focus on the development of functional additive systems applicable to all materials.
Technical Approach/Strategy - base oil

- There are synthetic base oil currently used for very challenging applications because of some desirable properties:
  - Stability over a wide temperature range.
  - Low volatility.
  - Inherent lubricity and wear protection attributes.
  - Available in wide range of viscosities.

- PAO- and Ester-based fluids meet these requirements.

- Develop composite base fluids consisting of very low viscosity components from PAO and Ester chemistries.
  - Optimize fluid mixture using thermodynamics principles
  - Characterize the rheological properties of fluid mixture
  - Evaluate tribological performance of composite base fluids
  - Determine the impact of additives on the tribological performance of new composite base fluid.
Technical Approach - Additives

- Current state-of-the-art lubricant additives perform several tribological functions via *surface chemical reactions*
  - Friction control (FM); wear prevention (AW); scuffing prevention (EP); chemical stability (AO); thermal dissipation
  - Often specific to ferrous surface and limited effectiveness

- New advanced lubricant additives based on *physical and/or chemical mechanisms* using colloidal additive technology to provide appropriate tribological attributes – can be used with different materials including coatings
  - Friction reducing particles – layer nano particles (MoS$_2$, h-BN, Graphite, Cu Ag…..)
  - Wear and scuffing performance – oxides and metallic nano particles (TiO$_2$, SiO$_2$, Ag, Cu, …..)
  - Chemical stability - (CaCO$_3$, Mg(OH)$_2$, …..)
  - Thermal dissipation – high conductivity nano particles (Cu, Ag, C, …..)

- Time control release attributes will be achieved by encapsulating the nano additives in an appropriate shell or surface layer – similar to pharmaceutical drug formulation
Technical Approach - additives

- Comprehensive tribological performance evaluation of Advanced current state-of-the-art commercial engine lubricants – performance benchmark for the project
  - Frictional attributes under different lubrication regimes
  - Wear behavior under different contact conditions
  - Scuffing performance under severe contact conditions

- Identify, design and synthesis of encapsulated colloidal particulate additive systems with desired tribological performance attributes: Friction reduction, wear protection and scuffing prevention

- Comprehensive tribological performance of candidate systems for various attributes
  - Effect of concentration
  - Combination of additives

- Mechanistic studies of candidate additives.
  - Optimization of the additive and base-fluid systems

- Technology transfer to appropriate stakeholders.
## FY14 and FY15 Project Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>03/15</td>
<td>Complete rheological properties characterization of composite fluid mixtures (completed)</td>
</tr>
<tr>
<td>06/15</td>
<td>Complete preliminary friction and wear performance evaluation of composite base fluid under unidirectional and reciprocating sliding (complete)</td>
</tr>
<tr>
<td>03/15</td>
<td>Characterize colloidal particulate additive candidate. (completed)</td>
</tr>
<tr>
<td>09/15</td>
<td>Complete initial tribological performance evaluation of some candidate colloidal additive systems as proof of concept (On going)</td>
</tr>
</tbody>
</table>
Technical Accomplishment and Progress: measurement of fluid mixture viscosity

Note: Percentages by volume

<table>
<thead>
<tr>
<th>%Ester ratio</th>
<th>Kinematic Viscosity (cSt)</th>
<th>Cold Crank Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40°C</td>
<td>100°C</td>
</tr>
<tr>
<td>0</td>
<td>17.8</td>
<td>4</td>
</tr>
<tr>
<td>30</td>
<td>17.8</td>
<td>4.06</td>
</tr>
<tr>
<td>40</td>
<td>17.9</td>
<td>3.95</td>
</tr>
<tr>
<td>50</td>
<td>17.9</td>
<td>4.01</td>
</tr>
<tr>
<td>60</td>
<td>18.3</td>
<td>4.16</td>
</tr>
<tr>
<td>70</td>
<td>18.4</td>
<td>4.34</td>
</tr>
<tr>
<td>100</td>
<td>19.6</td>
<td>4.33</td>
</tr>
</tbody>
</table>

Cold Crank Viscosity

Thermodynamics based Rheological properties predictive model under development.
- General applicability to any fluid mixture including fuel-oil mixture

HTHS Data Comparison

Viscosity (mPa-s) vs Temperature (°C)

Viscosity (cP) vs Shear [1/sec]
**Technical Accomplishment and Progress:**

**Traction Test**

<table>
<thead>
<tr>
<th>TEST CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rings</td>
</tr>
<tr>
<td>Roller</td>
</tr>
<tr>
<td>Oil</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Speed</td>
</tr>
<tr>
<td>Load</td>
</tr>
<tr>
<td>SRR</td>
</tr>
<tr>
<td>Test Length</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Data Logging Interval</td>
</tr>
</tbody>
</table>

**Significant traction (viscous losses) reduction in mixed fluids**
Preliminary Friction and Wear Performance Evaluation

**Reciprocating sliding - HFRR test**

- Load: **15N** $\sigma_{max}=0.99$ GPa.
- Speed: 1 cm/s (60 minutes) and variable: speed ramps-first and last 12 min: 0.1, 0.5, 1, 5, 10, 20 cm/s
- Diameter: **12-16 mm**
- Duration: **84 minutes**
- Temperature: **100°C**

**UNIDIRECTIONAL SLIDING - POD TEST**

- Load: **15N** $\sigma_{max}=0.99$ GPa.
- Speed: 60 rpm (60 minutes) and 2 min variable speed ramps from **0-300 rpm** at the beginning and end of test.
- Stroke length: **10 mm**
- Duration: **64 minutes**
- Temperature: **100°C**
Friction Results

Reciprocating Sliding

<table>
<thead>
<tr>
<th>% Ester in PAO4</th>
<th>Friction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.16</td>
</tr>
<tr>
<td>30</td>
<td>0.10</td>
</tr>
<tr>
<td>40</td>
<td>0.11</td>
</tr>
<tr>
<td>50</td>
<td>0.10</td>
</tr>
<tr>
<td>60</td>
<td>0.11</td>
</tr>
<tr>
<td>70</td>
<td>0.10</td>
</tr>
<tr>
<td>100</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Unidirectional Sliding

<table>
<thead>
<tr>
<th>% Ester in PAO4</th>
<th>Friction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.17</td>
</tr>
<tr>
<td>30</td>
<td>0.12</td>
</tr>
<tr>
<td>40</td>
<td>0.11</td>
</tr>
<tr>
<td>50</td>
<td>0.12</td>
</tr>
<tr>
<td>60</td>
<td>0.12</td>
</tr>
<tr>
<td>70</td>
<td>0.12</td>
</tr>
<tr>
<td>100</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Flat Wear Results

Surface protection against wear in fluid mixture – implication for anti-wear additives requirement

Reciprocating Sliding

Unidirectional Sliding

% Ester in PAO4

% Ester in PAO4
Technical Accomplishment and Progress: - Performance benchmark for new additive systems

- Established benchtop tribological performance benchmark for the project
  - Measured various performance attributes for several advanced state-of-art lubricants

![Coefficient of Friction Chart]

- E: Engine Oil
- Oils: E1, E2, E3, E4, E5, G1
TEM- characterization colloidal particles

TiO$_2$, SiO$_2$, ZrO$_2$-8Y
# Technical Accomplishment and Progress: Rheological properties - colloidal

## Kinematic Viscosity (40°C)

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Without Oleic Acid</th>
<th>With Oleic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Particle</td>
<td>18.2</td>
<td>18.2</td>
</tr>
<tr>
<td>Ag Polymer Coated</td>
<td>18.3</td>
<td>18.3</td>
</tr>
<tr>
<td>Graphite</td>
<td>18.4</td>
<td>18.4</td>
</tr>
<tr>
<td>Al</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>BN</td>
<td>18.8</td>
<td>18.8</td>
</tr>
<tr>
<td>Si3N4</td>
<td>18.6</td>
<td>18.6</td>
</tr>
<tr>
<td>SiO2</td>
<td>18.7</td>
<td>18.7</td>
</tr>
<tr>
<td>Al2O3</td>
<td>19.1</td>
<td>19.1</td>
</tr>
<tr>
<td>ZrO2</td>
<td>18.9</td>
<td>18.9</td>
</tr>
<tr>
<td>TiO2</td>
<td>18.5</td>
<td>18.5</td>
</tr>
<tr>
<td>Cu in Organic Media</td>
<td>18.4</td>
<td>18.4</td>
</tr>
</tbody>
</table>

*0.1% concentration of particulate additives*
Initial friction and wear characterization

TiO2

Wear = $3.2396 \times 10^3 \mu m^3$

Wear = $-0.0249932 \times 10^3 \mu m^2$

Y Profile: $\Delta X = 0.6440 \text{ mm}, \Delta Z = 0.1614 \text{ mm}$

Y Profile: $\Delta X = 0.6440 \text{ mm}, \Delta Z = 35.4116 \text{ nm}$
Range of tribological performance for several systems
Technical Accomplishment and Progress: - Effect of encapsulator

**Ball Wear**
- 0.1% TiO₂

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>Cap 1</th>
<th>Cap 2</th>
<th>Cap 3</th>
<th>Cap 4</th>
<th>Cap 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Wear ($10^3$ μm³)</td>
<td>800</td>
<td>200</td>
<td>400</td>
<td>200</td>
<td>600</td>
<td>800</td>
</tr>
</tbody>
</table>

**Flat Wear/µm**
- 0.1% TiO₂

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>Cap 1</th>
<th>Cap 2</th>
<th>Cap 3</th>
<th>Cap 4</th>
<th>Cap 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat Wear ($10^3$ µm²)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Coefficient of Friction**
- 0.1% TiO₂

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>Cap 1</th>
<th>Cap 2</th>
<th>Cap 3</th>
<th>Cap 4</th>
<th>Cap 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of Friction</td>
<td>0.25</td>
<td>0.20</td>
<td>0.15</td>
<td>0.15</td>
<td>0.20</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Tribofilm- preliminary analysis TEM

Tribo films from colloidal additives similar to ones from current advanced lubricants
Summary

- Mixed base fluids all showed superior performance in terms of friction and wear compared to a monolithic PAO fluid under both unidirectional and reciprocating sliding.
  - Attributed to better surface activity of ester as indicated by the formation of protective durable surface films.
  - Thermodynamic modeling of mixed fluid properties underway.

- Identified several candidate materials for colloidal additive system for lubricants.
  - Minimal effect on the viscosity of base fluid – candidate for low viscosity oils.
  - Tribological performance equivalent or superior to nano systems and current advanced lubricants.

- Several effective encapsulation agents identified for the colloidal additive systems.
  - Pathway for optimization of time release behavior.
Future Plans

- Development of thermodynamic model for fluid mixture viscosity and other rheological properties.
- Mechanistic study of tribological performance enhancement for mixed fluids.
  - Characterization of surface films formed during tribological contact.
- Evaluate impact of additives on tribological performance of mixed fluids.
- Tribological performance evaluation of colloidal additives
- Synthesize colloidal particles with different surface layers for different additive functions.
  - Characterize the structure of the optimized layer particles
  - Tribo films by design from colloidal particulate systems
  - Conduct comprehensive tribological performance evaluation
  - Determine the operating lubrication mechanisms and the role of the additives
- Eventual technology transfer to appropriate stake holder.
Project Collaborations - Research activities include collaborations with leading industry and academic partners

- **Consortia Memberships**
  - Member of the MIT Lubrication Consortium
  - Member of the OSU Gear Consortium

- **Collaborations with Industry on Funding Opportunity Announcements (FOAs)**
  - FOA 239 (Cummins and Lubrizol)
  - FOA 793 (Ford, and NWU)
  - FOA 991 (Ricardo, Isuzu, ZYNP, Infineum)

- **CRADAs (which have led to focused follow-on projects)**
  - Ricardo
  - Pixelligent
  - XG-Sciences

- **Funded Research (business sensitive)**
  - Vehicle and Engine OEMs
  - Suppliers
  - Lubricant & Additive OEMs
  - Small Businesses (SBIR, STTR)

- **Topics (2-way interactions)**
  - Failure analysis
  - Tribological evaluation (friction and wear)
  - Surface characterization
  - Friction modeling
  - Oil formulation
  - Additive formulation
  - Coatings
    - DLCs, Fe-Boriding, Nitrides
  - Sample/Components for testing
    - Engine blocks
    - Liners, Rings, Pistons
    - Bearings
Technical Backup slides
Prediction of viscosity of mixed fluids

A model developed based on Eyring’s absolute rate theory approach and the UNIQUAC equations

Eyring’s rate theory

\[ \eta = \frac{hN}{v} \exp\left(\frac{\Delta g^\ddagger}{RT}\right) \]  \hspace{1cm} (1)

A correction/excess term is added to account for non-ideal behavior

\[ \Delta g^\ddagger = \Delta g_{\text{ideal}}^\ddagger + \Delta g_E^\ddagger \]  \hspace{1cm} (2)

\[ \frac{\Delta g_{\text{ideal}}^\ddagger}{RT} = \sum_i x_i \ln(\eta_i v_i^0) - \ln(hN) \]  \hspace{1cm} (3)

\[ \frac{\Delta g_E^\ddagger}{RT} = \sum_{i=1}^{N_{\text{SOL}}} x_i \ln\left(\frac{\phi_i}{x_i}\right) + \frac{1}{2} \sum_{i=1}^{N_{\text{SOL}}} q_i x_i \ln\left(\frac{\theta_i}{\phi_i}\right) - \sum_{i=1}^{N_{\text{SOL}}} x_i \sum_{k=1}^{N_{\text{SOL}}} \theta_i \psi_{ki} \]  \hspace{1cm} (4)

This model has been applied to several hundred binary mixtures

\[ \eta = \text{Kinematic Viscosity (mm}^2\text{ s}^{-1}) \]

\[ T = 303.15 \text{ K} \]

0.1 MPa

methanol + ethanol

\[ v_i^0 = \text{molar volume of pure liquid } i \]

\[ x_i = \text{mole fraction of component } i \]

\[ \phi_i = \text{coordination number} \]

\[ N_{\text{SOL}} = \text{number of solvents in the mixture} \]

\[ q_i = \text{surface area parameter} \]

\[ \theta_i = \text{surface area fraction} \]

\[ \psi_{ki} = \text{UNIQUAC interaction parameter between species } k \text{ and } i \]

\[ \eta_i = \text{pure component } i \]
<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Size</th>
<th>Purity</th>
<th>Comments (Shape, coatings etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>5-15 nm</td>
<td>99.8%</td>
<td>Surface modified, hydrophobic and oleophilic</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5-10 nm</td>
<td>99.5%</td>
<td>Rutile, Silane Coated</td>
</tr>
<tr>
<td>ZrO₂-8Y</td>
<td>20nm</td>
<td>Y₂O₃-13.5%, ZrO₂-86%</td>
<td>Near spherical morphology</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5nm</td>
<td>99.9%</td>
<td>Gamma, Fibrous morphology</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>20nm</td>
<td>99%</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Poly Coated Ag</td>
<td>15nm</td>
<td>99.9% of Ag Composition: 25% Ag+75% Polymer</td>
<td>Self dispersible</td>
</tr>
<tr>
<td>Al</td>
<td>18nm</td>
<td>99.9%</td>
<td>Spherical morphology</td>
</tr>
<tr>
<td>Graphite</td>
<td>3-4nm</td>
<td>93%</td>
<td>Spherical Morphology, hexagonal carbon</td>
</tr>
<tr>
<td>BN White</td>
<td>10nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu in Organic Media</td>
<td>5-7nm</td>
<td>14% Cu</td>
<td>Oil soluble, dispersible, Lubricants Additive</td>
</tr>
</tbody>
</table>