Research on Fuels & Lubricants

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Penn State’s Slippery Bunch:

- 1950’s  Dew Line Lubricants, New Base Oil & Additive Technology
- 1960’s  SR 71 Blackbird Hydraulic Fluids, Super Refined Lubricants (Type II)
- 1970’s  Oxidation, Greases, Metals
- 1980’s  VPO, Adiabatic Engine, MeOH Oils
- 1990’s  Environmentally Friendly Fluids, Extended Drain Oils
Current Projects

- Fuel Studies
  - DME
  - Biodiesel
  - ULSF
- Vegetable Oils
- High Temperature Liquid Lubricants
- Coatings & Lubricants
- Role of Chemical Structure
Penn State “Green” Project

1. Over 200 pieces of farm & construction equipment on campus.
2. Conversion to Environmentally Friendly Lubricants initiated.
3. Use of Biodiesel in farm equipment.
**FUELS**

**Diesel Fuels**
- Petroleum cut boiling ~ 282-338°C, #2, LSDF and ULSDF
  - 300 ppm S
  - 32 ppm S
  - ULSD (< 15ppm S)

**Biodiesel Fuels**
- Blends of methyl esters made from vegetable oils

**Dimethyl Ether**
- Converted from Syngas

**Distillation**
- Hydrocarbon mixture

**Soybeans**

**+ ROH**
- catalyst

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DME Research

DME is environmentally benign
- Decomposes rapidly
- Doesn’t harm ozone layer

DME Methane + H2 + CO

Reduces diesel engine emissions
- Addition of oxygen into combustion zone

Engine and Vehicle Tests
- Problems include low viscosity (wear), high vapor pressure, and material compatibility

Laboratory Tests
- Viscosity Studies
- Injector Studies
- O-Ring Studies
Fuel Injector Studies

Modified Cameron – Plint Machine

Test Pins

New  DME  SCUFFED

Fuel Injector Pin

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Biodiesel Fuel Studies

Previous work involved study of VPO of diesel and biodiesel fuels in pilot plant (10).

Demonstrated in laboratory tests that addition of oxygen to biodiesel resulted in improvement in friction.

Run #1
Temp- 325°C
Feed Rate- 1000 g/hr
$O_2$/Feed Mole Ratio- 1.0

Run #2
Temp- 375°C
Feed Rate- 1000 g/hr
$O_2$/Feed Mole Ratio- 1.0

Low Sulfur & Oxidized Diesel Fuels

![Graph showing friction coefficient over time for Low Sulfur Diesel, Ox. Diesel Run #1, and Ox. Diesel Run #2.](image-url)
Friction Traces for ULSDFs
Fuel Deposit Tests

Micro-oxidation test

10ml of test fuel into glass test tube
One stainless steel pan
Heat to 150°C for 7 days
Weigh and characterize deposits on pan

Fuel also filtered through Al column to remove additives and analyzed

Test Fuels

A,B,C  Ultra low sulfur fuels, different manufacturers
D     Low sulfur diesel
E     Kerosene
G     #2 diesel
Fuel Deposits

Progressively less deposits as B is filtered

Order of deposit thickness, most to least:
B >> A > D > C > G > E

Progressively less deposits as G is filtered (not as dramatic as B)

*Filtered fuel shows little or no deposits on walls of glass micro-oxidation tubes as well as on coupons
Fuel B significantly different - additive?

Fuel C, D similar to A

GC Analyses - Fuels

Fuel A
Fuel B
Fuel G
Does the Chemical Structure of the Base Fluid affect its effectiveness in protecting the surface against wear?
Effect of Structure

- Alcohol + Acid $\xrightarrow{\text{catalyst, heat}}$ Ester + Water

To evaluate structure effect use same acid (2-ethylhexanoic) and different alcohols:

- Neopentyl Glycol $(\text{CH}_3)_2\text{C}($CH$_2$OH)$_2$
- Trimethylol propane $\text{CH}_3\text{CH}_2\text{C}($CH$_2$OH)$_3$
- Pentaerytritol $\text{C}($CH$_2$OH)$_4$

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Effect of Acid Chain Length on Wear

- Trimethylol propane = alcohol

**Acids:**
- D = nC5
- E = nC7
- F = mixture of nC8 & C10

Diagram: 
- Ester D
- Ester E
- Ester F
Wear Index =

\[(\text{Total Carbons})(\text{Effective Chain Length})\]
\[(\text{Polar Value + Branching Value})\]

where:
Total Carbons = total carbons in the molecule

Effective Length = longest free chain of carbons available to form a film.

Polar Value = No. of carboxyl groups + No. of hydroxyl groups

Branching Value = \((0.5 \times \text{No. of branches}) + \text{No. of double bonds}\).
WEAR INDEX vs WEAR RATE

TEST COND: 40kg, 75°C, 600rpm, 30min

$R^2 = 0.7934$
EFFECT of CHAIN LENGTH on FRICTION COEF.

TEST CONDITIONS: 40 kg, 75 C., 600 rpm, 30

$R^2 = 0.9622$
Test Methods

[Diagram showing a test method setup with labeled parts: Ball Pot, Torque Arm, Stationary Balls, Rotating Ball, Heating Block, Thermocouple, and a load application mechanism.]
## Test Conditions

<table>
<thead>
<tr>
<th>Four Ball Wear Tester:</th>
<th>Pin – on – Disc:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ANSI 52100 stainless steel balls</strong></td>
<td>Variable Speed</td>
</tr>
<tr>
<td><strong>Test Time:</strong></td>
<td>Variable Load</td>
</tr>
<tr>
<td>30 min Run-in</td>
<td>This study:</td>
</tr>
<tr>
<td>30 min Steady State</td>
<td>10 RPM</td>
</tr>
<tr>
<td>30 min Surface Eval’n</td>
<td>20 N</td>
</tr>
<tr>
<td><strong>Test temp. = RT, 60°C, 75°C</strong></td>
<td>Room Temp.</td>
</tr>
<tr>
<td><strong>Speed = 600, 1200 RPM</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Loads = 1,10, 40 Kg</strong></td>
<td></td>
</tr>
</tbody>
</table>
## Properties of Test Oils

<table>
<thead>
<tr>
<th>Oil Properties</th>
<th>Oil A</th>
<th>Oil B</th>
<th>Oil C</th>
<th>OIL D</th>
</tr>
</thead>
<tbody>
<tr>
<td>cSt Visc @ 100°C (ASTM D 445)</td>
<td>3.9</td>
<td>4.99</td>
<td>8.29</td>
<td>24.4</td>
</tr>
<tr>
<td>cSt Visc @ 40°C</td>
<td>16.9</td>
<td>28.8</td>
<td>66.8</td>
<td>215</td>
</tr>
<tr>
<td>Viscosity Index (ASTM D2270)</td>
<td>123</td>
<td>97</td>
<td>91</td>
<td>120</td>
</tr>
<tr>
<td>Flash Point, °C (ASTM D 92)</td>
<td>219</td>
<td>226</td>
<td>254</td>
<td>&gt;&gt;200</td>
</tr>
</tbody>
</table>
Effect of “Chain Length” of Hydrocarbon Oils on Wear – 4Ball Test

![Graph showing the effect of different oils on wear during various test segments.]
Effect of Oil “Chain Length” – Tribometer (CSEM)
Friction coefficient of HMW Synth - Veg Oil without antiwear additive

Pin-on-Disc Avg f = 0.066

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Effect of “Chain Length” of Hydrocarbon Oils on Wear – 4Ball Test vs Tribometer

\[ R^2 = 0.7764 \]
Effect of Double Bonds – Veg Oils

- ESBO
- SBO
- HOSBO

△ Wear, mm

Run-in | Steady State | Film Eval
--- | --- | ---
0.3 | 0.2 | 0.1
0.25 | 0.15 | 0.1
0.2 | 0.1 | 0.1
0.15 | 0.05 | 0.05
0.1 | 0.05 | 0.05
0.05 | 0.05 | 0.05
0 | 0 | 0

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Additive Effectiveness - Additive A

- Run-in
- Steady State
- Film Eval.

Graph showing wear in mm for different conditions and additives.
Effect of Unsaturation - Additive A

![Bar chart showing wear measurements for different conditions and additives.](image-url)

- **Run-in**: Comparison of SBO, HOSBO, and SBO + Add A.
- **Steady State**: Similar comparison with an increase in wear for HOSBO + Add A.
- **Film Eval.**: Increase in wear for all conditions, with a notable increase for HOSBO + Add A.

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Additive Effectiveness - Additive B

- Run-in
- Steady State
- Film Eval.

SBO
+ Add B
ESBO
+ Add B
Effect of Unsaturation - Additive B

- Run-in
- Steady State
- Film Eval.

Categories: SBO, + Add B, HOSBO, + Add B
Additive Effectiveness - Additive C

- SBO
- + Add C
- ESBO
- + Add C

Δ Wear, mm

Run-in | Steady State | Film Eval.
Effect of Unsaturation - Additive C

- SBO
- + Add C
- HOSBO
- + Add C

Wear, mm

Run-in | Steady State | Film Eval.

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Summary

- EFF & L - research studies & demonstration projects.
- Oxygenated Alternative Fuels - reduce particulates.
- DME - potential wear problems.
- VPO Biodiesel - effective f & wear additive.
- ULSF’s – wear, deposits, filter plugging.
- Chemical structure of base fluids and additives - significant factor in future lubricant formulation.
- New test methods - key to understanding surface interactions. (Optical, Advanced Photon Source, etc.)
- Surface engineering–materials, coatings & lubricants.
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- Kraipat Cheenkachorn – Vegetable Oils
- David Weller – Chemical Characterization

**Northwestern University:**
- Ashlie Martini - Pin-on-disc studies,
- Mark Sturino - Pin-on-disc studies, Optical Microscopy
Is Tribology Important?

Lack of Tribological Solutions results in Big Business:

- 1980 Survey - Over 20 Billion lost due to friction and wear annually
  ASME Research Committee, circa 1980

- 1995 - Over 1.5% of the gross national product is lost due to friction and wear
  Amato, Ivan, “Better ways to Grease Industry’s Wheels” Fortune, Sept 1995; 256 [B]-256[K]