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Research on Fuels & Lubricants

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Diesel Engine Emissions Reduction Conference
Newport, RI
August 24-28, 2003

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

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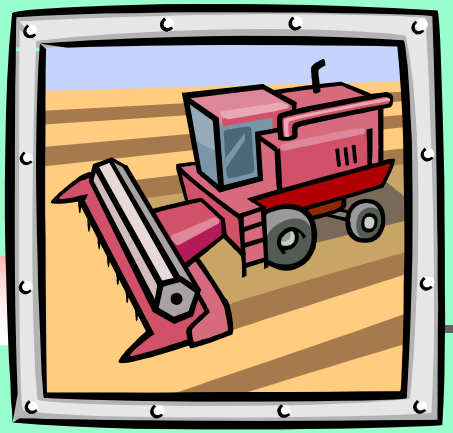

Penn State "Green" Project

1. Over 200 pieces of farm & construction equipment on campus.
2. Conversion to Environmentally Friendly Lubricants initiated.
3. Use of Biodiesel in farm equipment.
4. Conversion of waste oils to Biodiesel – Undergraduate Engineering Project

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FUELS

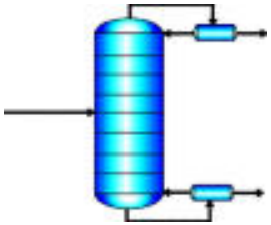
Diesel Fuels

Petroleum cut boiling ~ 282-338°C, #2, LSDF and ULSDF

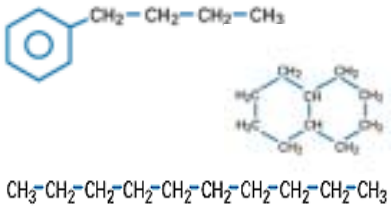
300 ppm S

32 ppm S

ULSD (< 15ppm S)



Distillation



Hydrocarbon mixture

Soybeans

+ ROH $\xrightarrow{\text{catalyst}}$

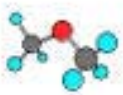
Biodiesel Fuels

Blends of methyl esters made from vegetable oils

Dimethyl Ether

Converted from Syngas

Hydrocarbon $\longrightarrow$ Syngas $\longrightarrow$ DME



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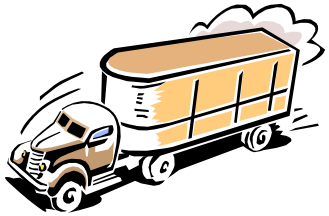
DME Research

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

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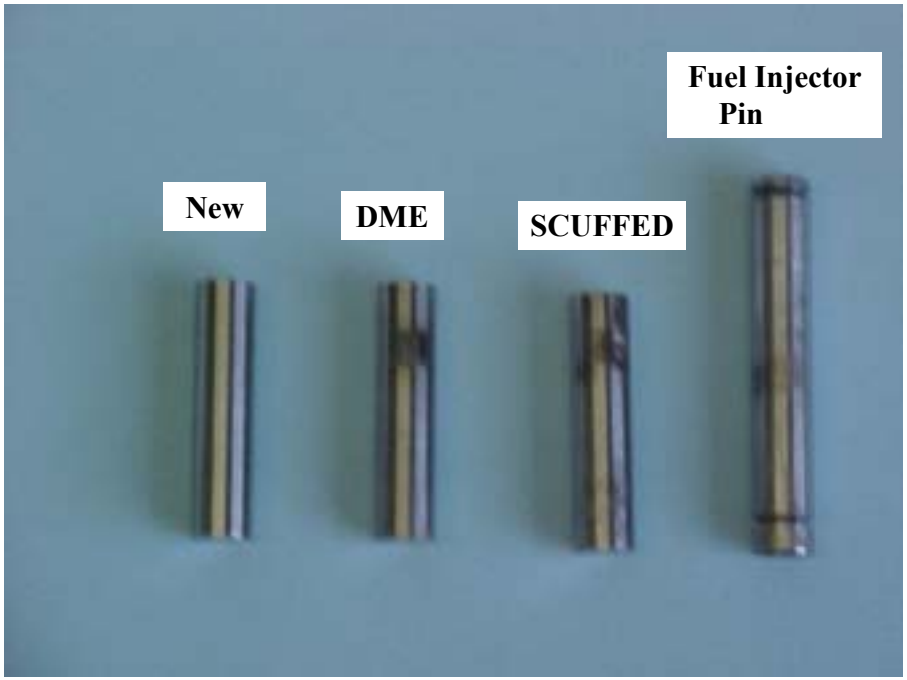
Modified Cameron – Plint Machine

Test Pins



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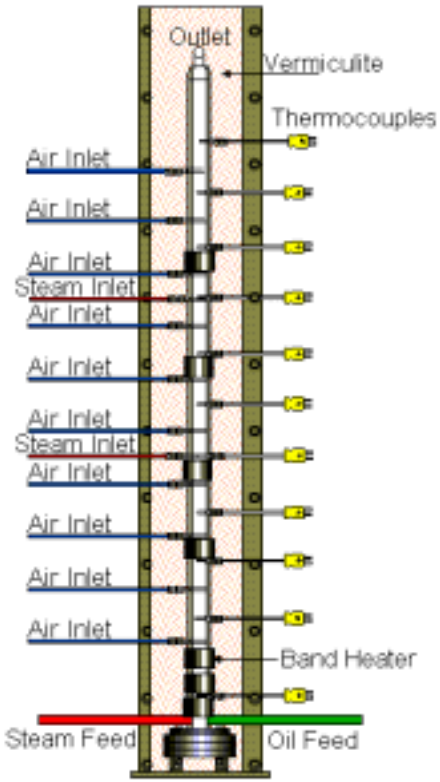
Biodiesel Fuel Studies

Previous work involved study of VPO of diesel and biodiesel fuels in pilot plant [10]

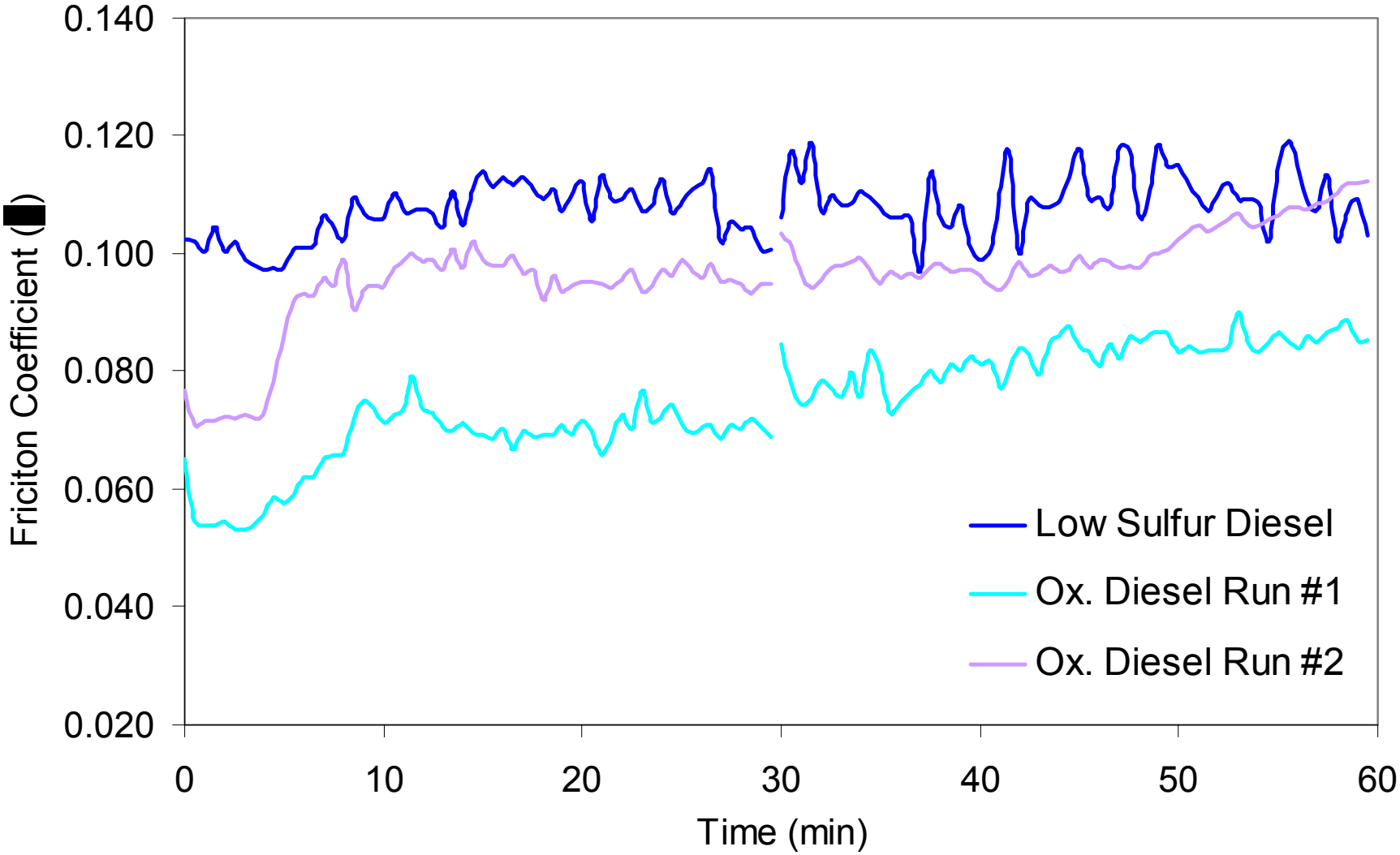
Demonstrated in laboratory tests that addition of oxygen to biodiesel resulted in improvement in friction

Run #1	Run #2
Temp- 325°C	Temp- 375°C
Feed Rate- 1000 g/hr	Feed Rate- 1000 g/hr
O_2/Feed Mole Ratio- 1.0	O_2/Feed Mole Ratio- 1.0



(10) Wain, K. Perez, J. " Oxidation of Biodiesel Fuels for Improved Fuel Lubricity" Proceedings of the Internal Combustion Engine Division, Lubrication and Friction Committee ASME Rockford, IL #2002-ICE-447 (2002)

Low Sulfur & Oxidized Diesel Fuels



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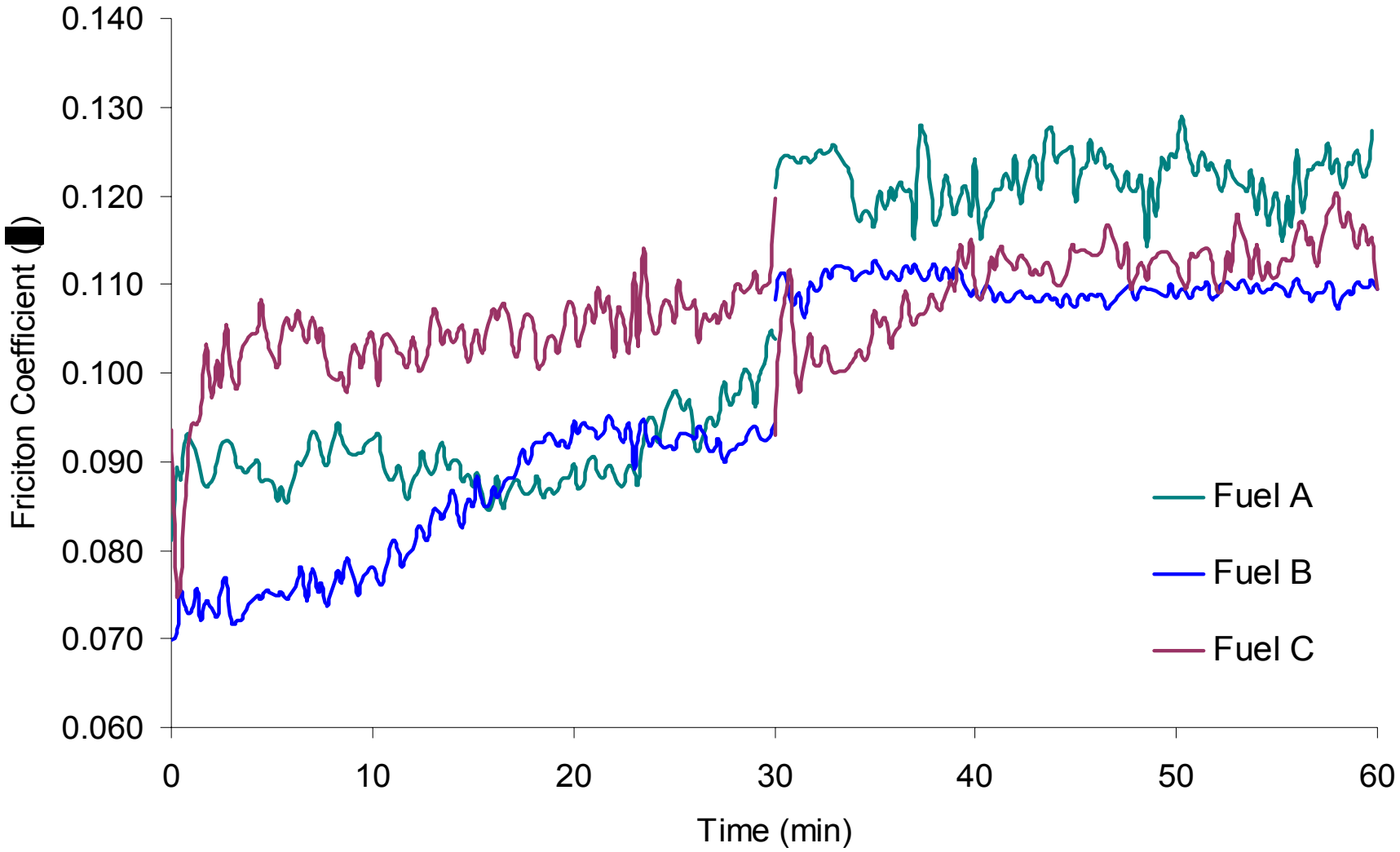
Friction Traces for ULSDFs



Fuel Deposit Tests

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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

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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

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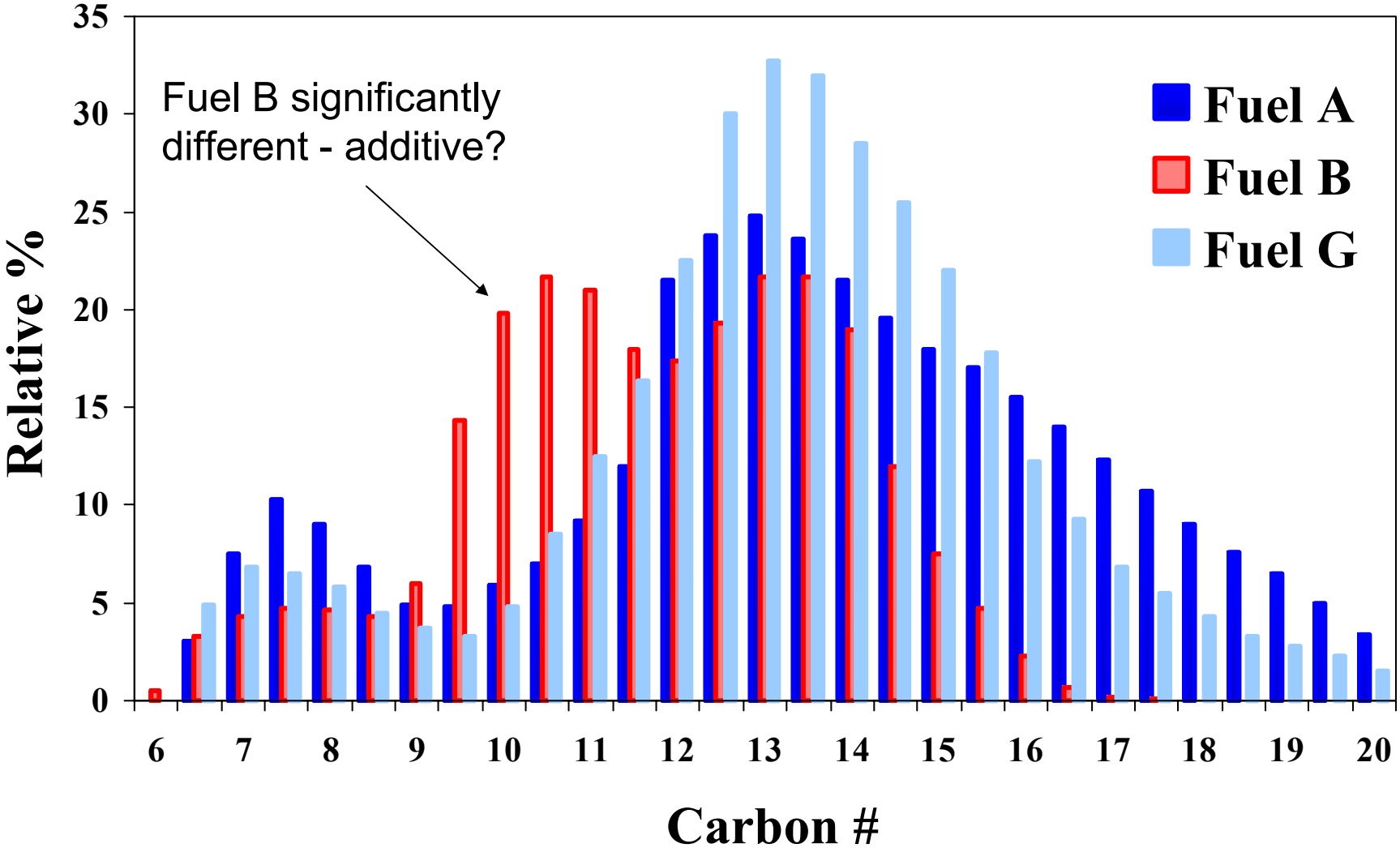
GC Analyses - Fuels



Fuel C, D similar to A

LUBRICANT RESEARCH

Does the Chemical Structure of the Base Fluid affect its effectiveness in protecting the surface against wear?

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Effect of Structure

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

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

- **Neopentyl Glycol** $(CH_3)_2C(CH_2OH)_2$
- **Trimethylol propane** $CH_3CH_2C(CH_2OH)_3$
- **Pentaerytritol** $C(CH_2OH)_4$

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Effect of Acid Chain Length on Wear

- **Trimethylol propane = alcohol**

<u>Acids</u>:

D = nC5

E = nC7

F = mixture of nC8 & C10

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Wear Index =

$$\frac{\text{(Total Carbons)(Effective Chain Length)}}{\text{(Polar Value + Branching Value)}}$$

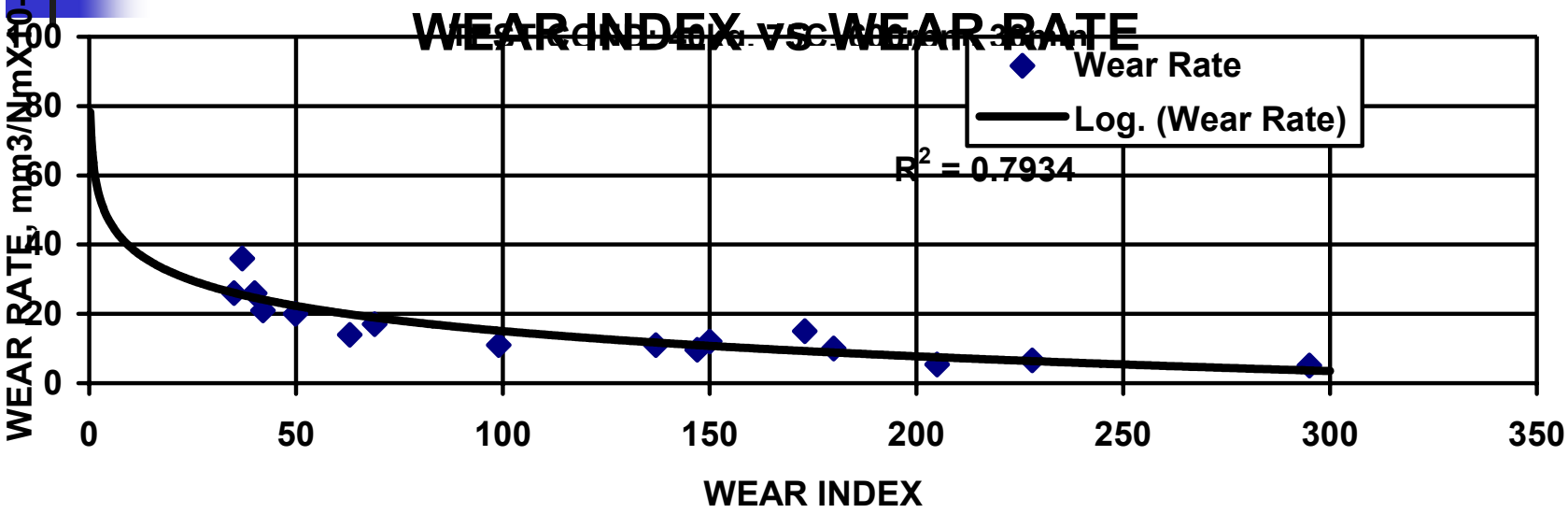
where:

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 x No. of branches) + No. of double bonds.



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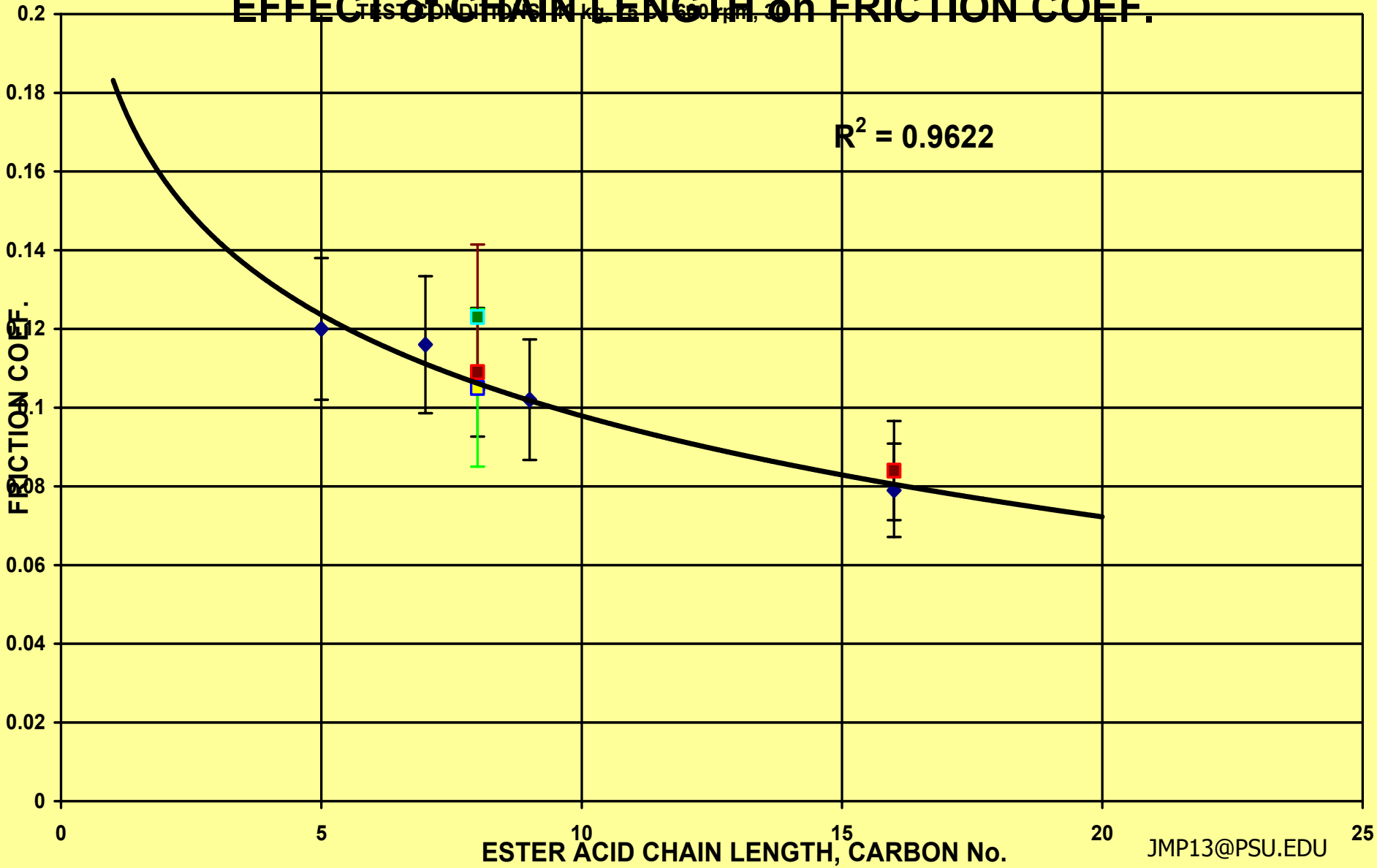
EFFECT of CHAIN LENGTH on FRICTION COEF.



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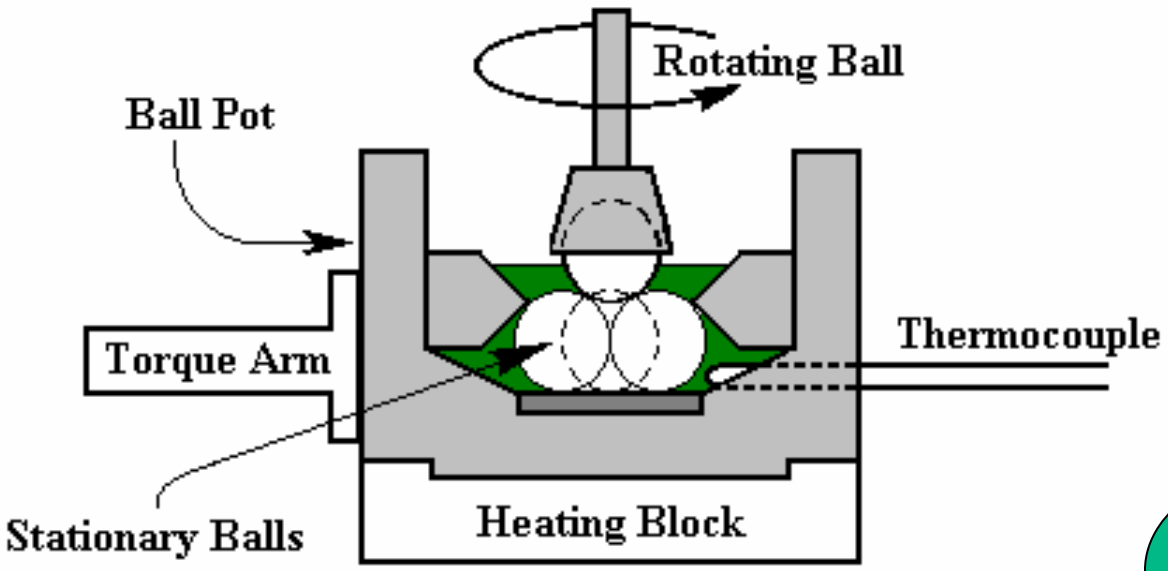
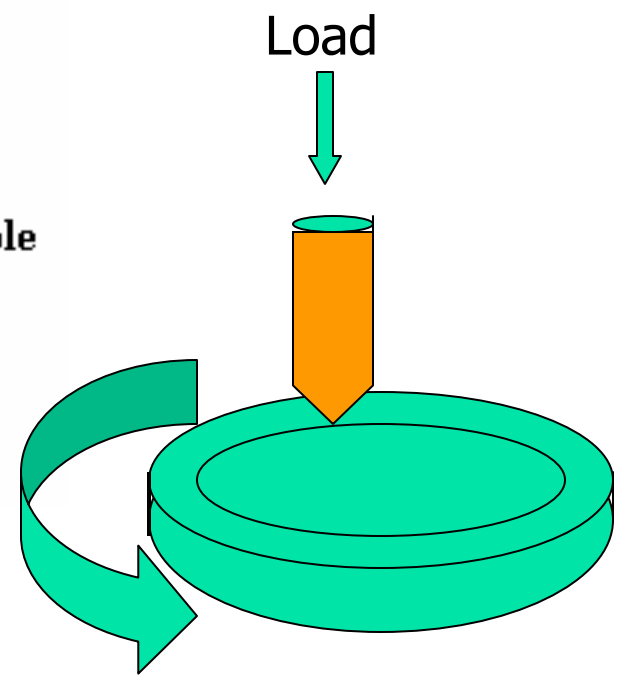
Test Methods





Test Conditions

Four Ball Wear Tester:	Pin – on – Disc:
ANSI 52100 stainless steel balls **Test Time:** **30 min Run-in** **30 min Steady State** **30 min Surface Eval'n** **Test temp. = RT, 60°C, 75°C** **Speed = 600, 1200 RPM** **Loads = 1,10, 40 Kg**	Variable Speed Variable Load This study: 10 RPM 20 N Room Temp.

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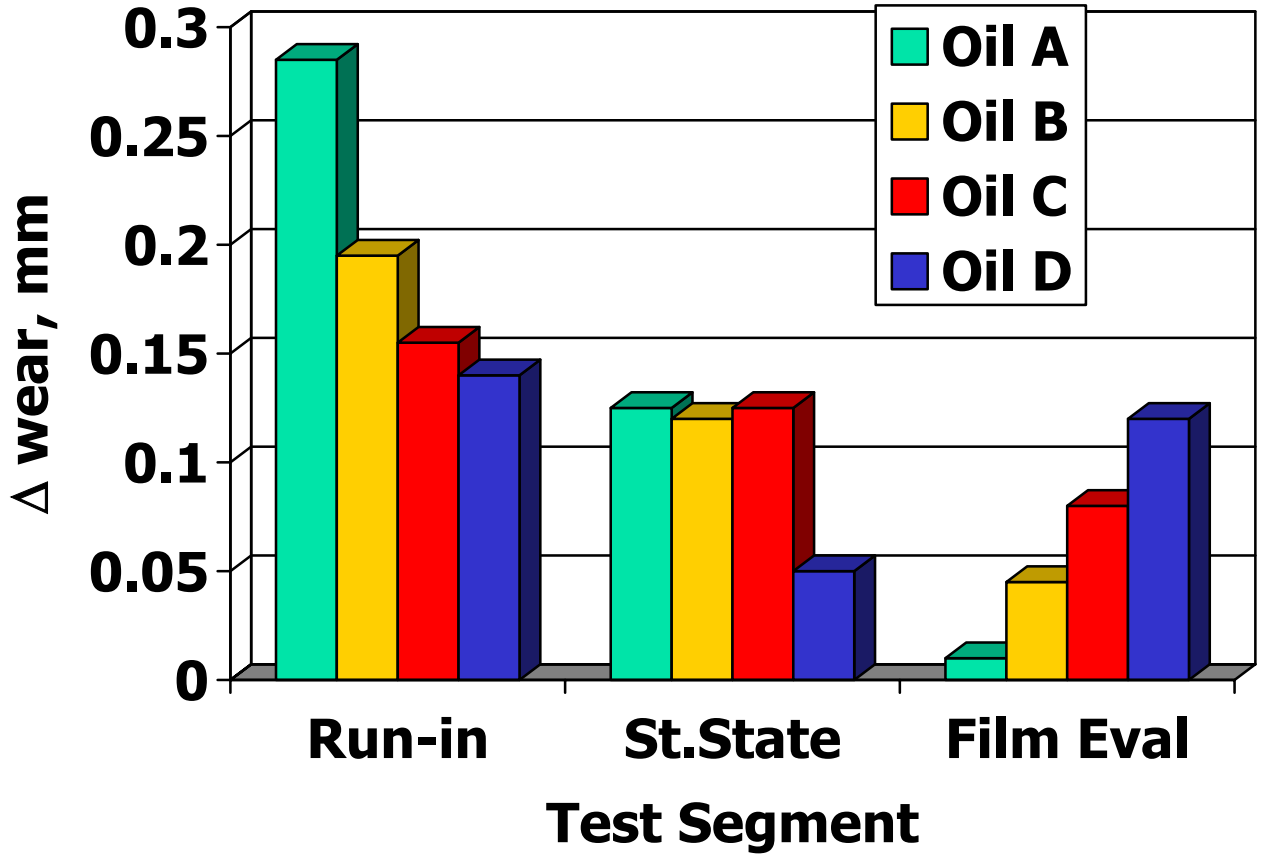
Properties of Test Oils

Oil Properties → ↓	Oil A	Oil B	Oil C	OIL D
cSt Visc @ 100 ^{o}C (ASTM D 445)	3.9	4.99	8.29	24.4
cSt Visc @ 40 ^{o}C	16.9	28.8	66.8	215
Viscosity Index (ASTM D2270)	123	97	91	120
Flash Point, ^{o}C (ASTM D 92)	219	226	254	>>200

Effect of "Chain Length" of Hydrocarbon Oils on Wear – 4Ball Test



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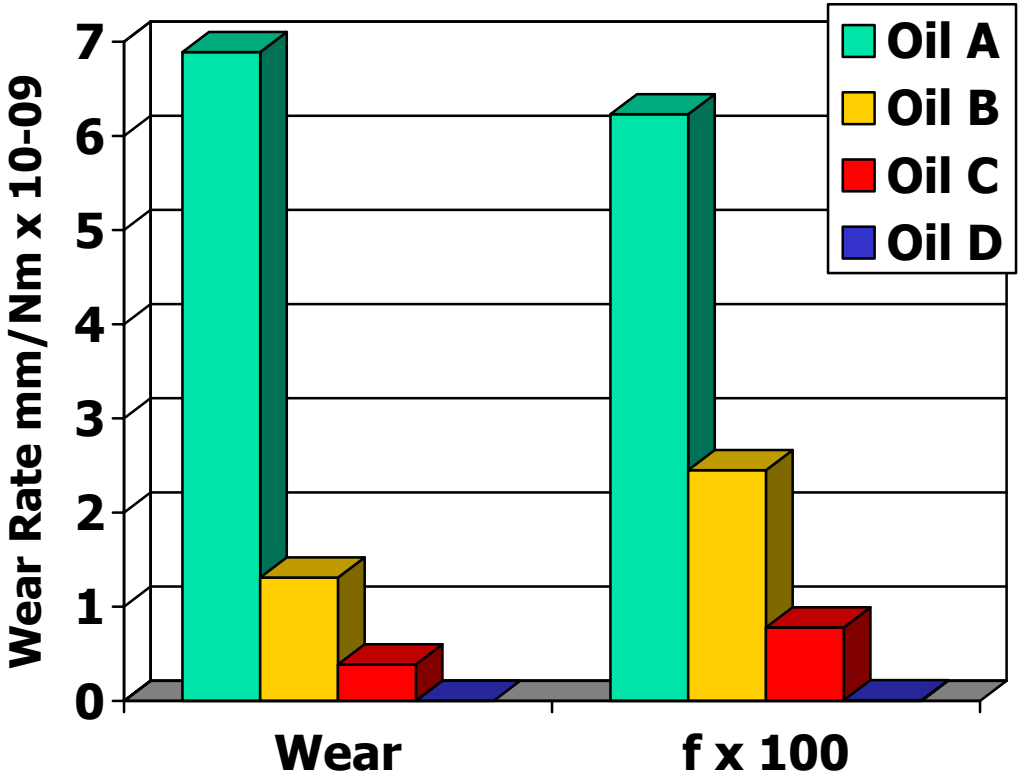
Effect of Oil "Chain Length" – Tribometer (CSEM)



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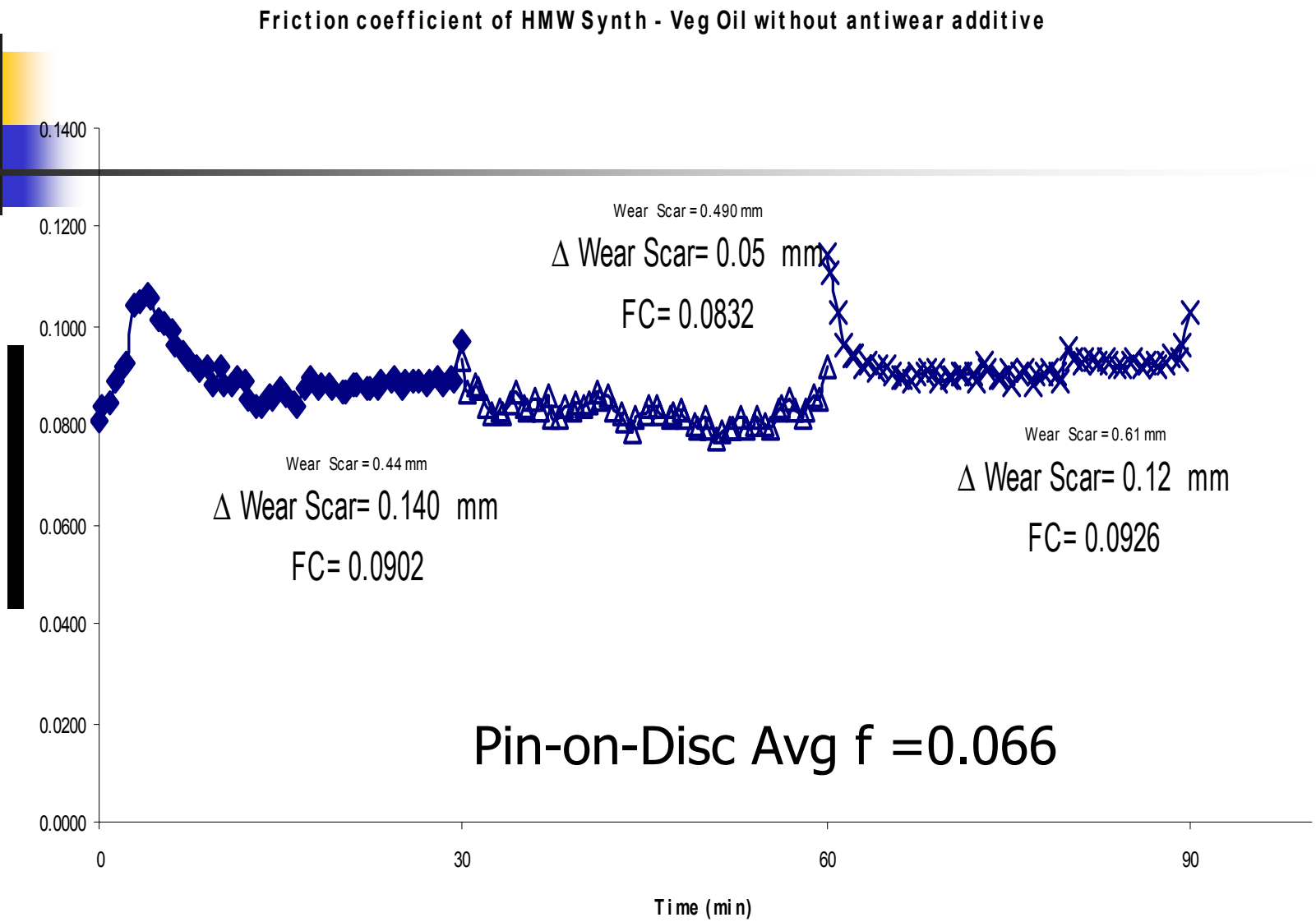

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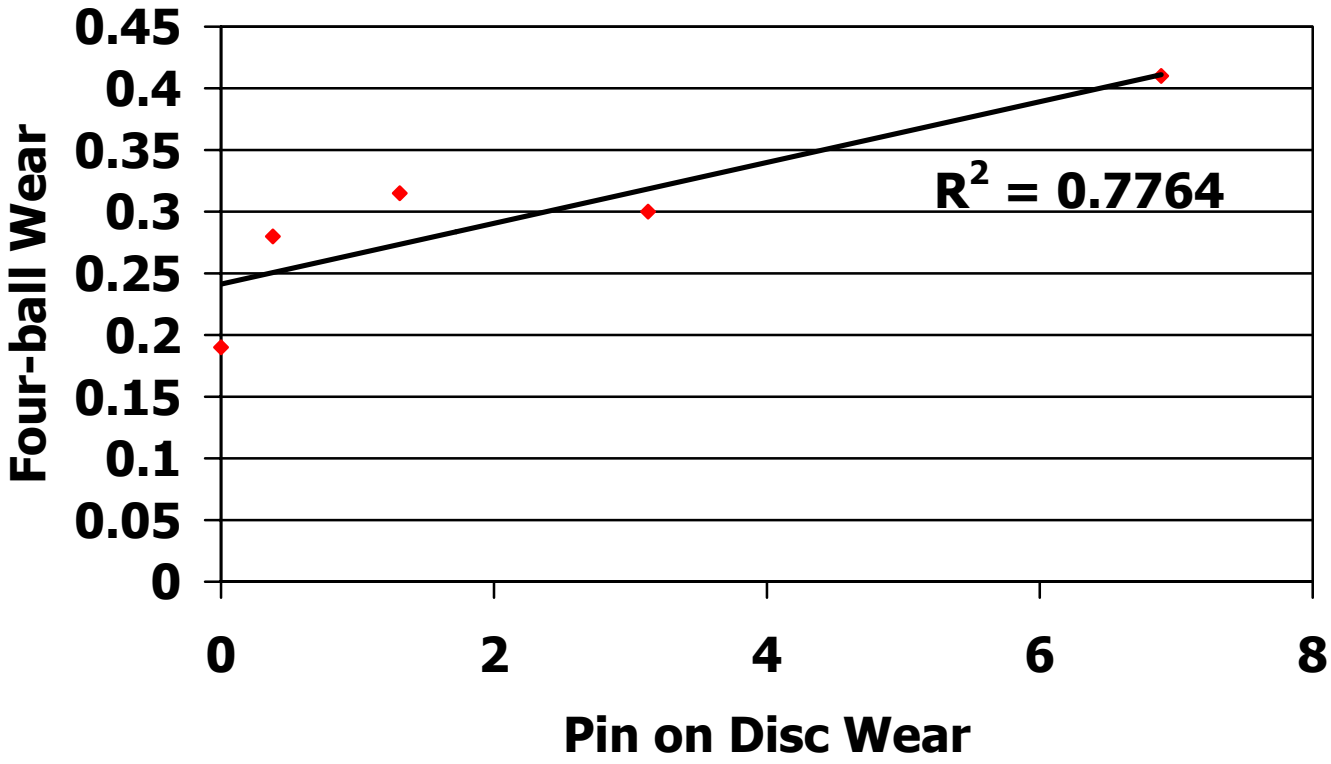
Effect of "Chain Length" of Hydrocarbon Oils on Wear – 4Ball Test vs Tribometer



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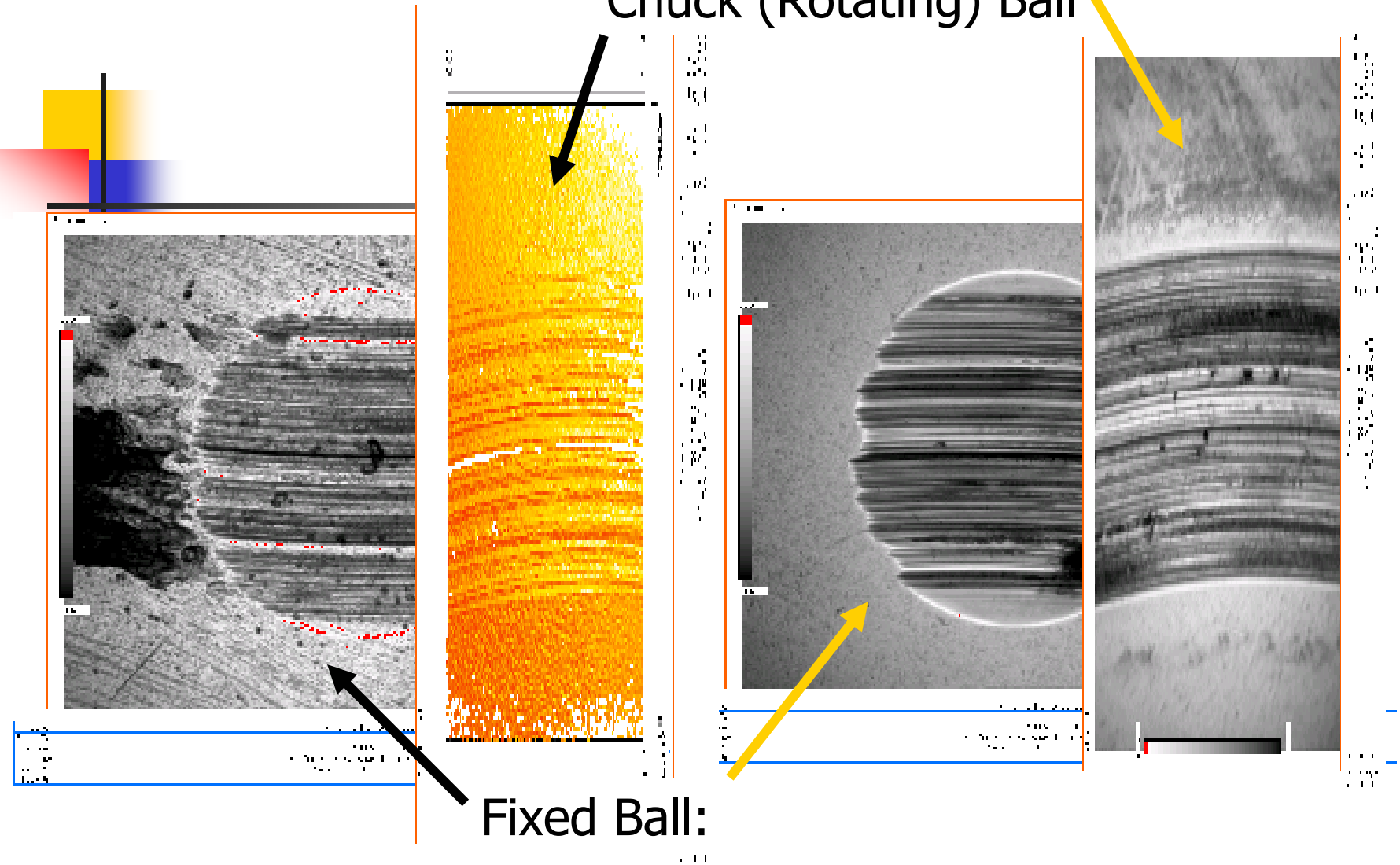
Chuck (Rotating) Ball



Fixed Ball:

Before Cleaning

After Cleaning

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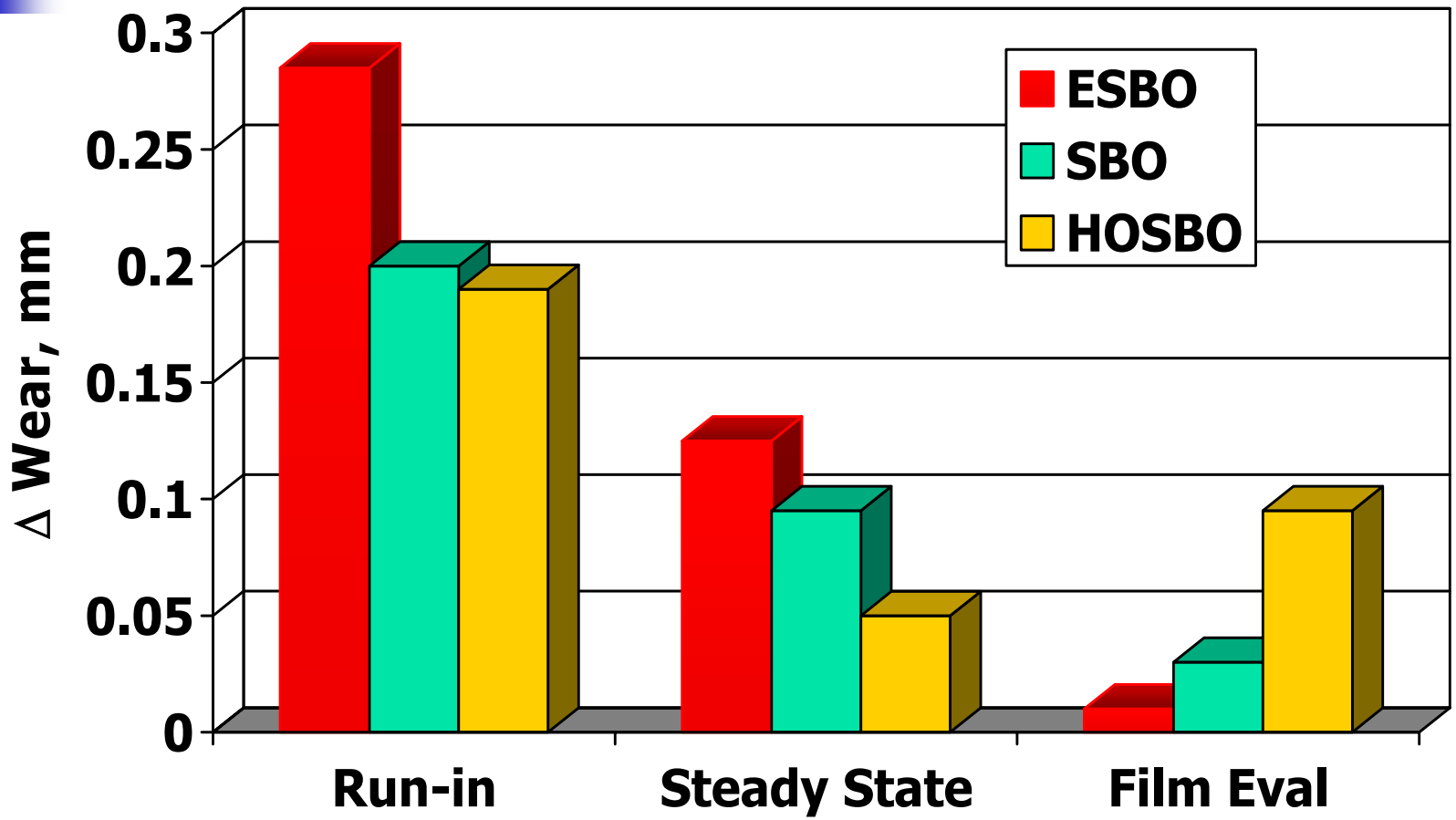
Effect of Double Bonds – Veg Oils



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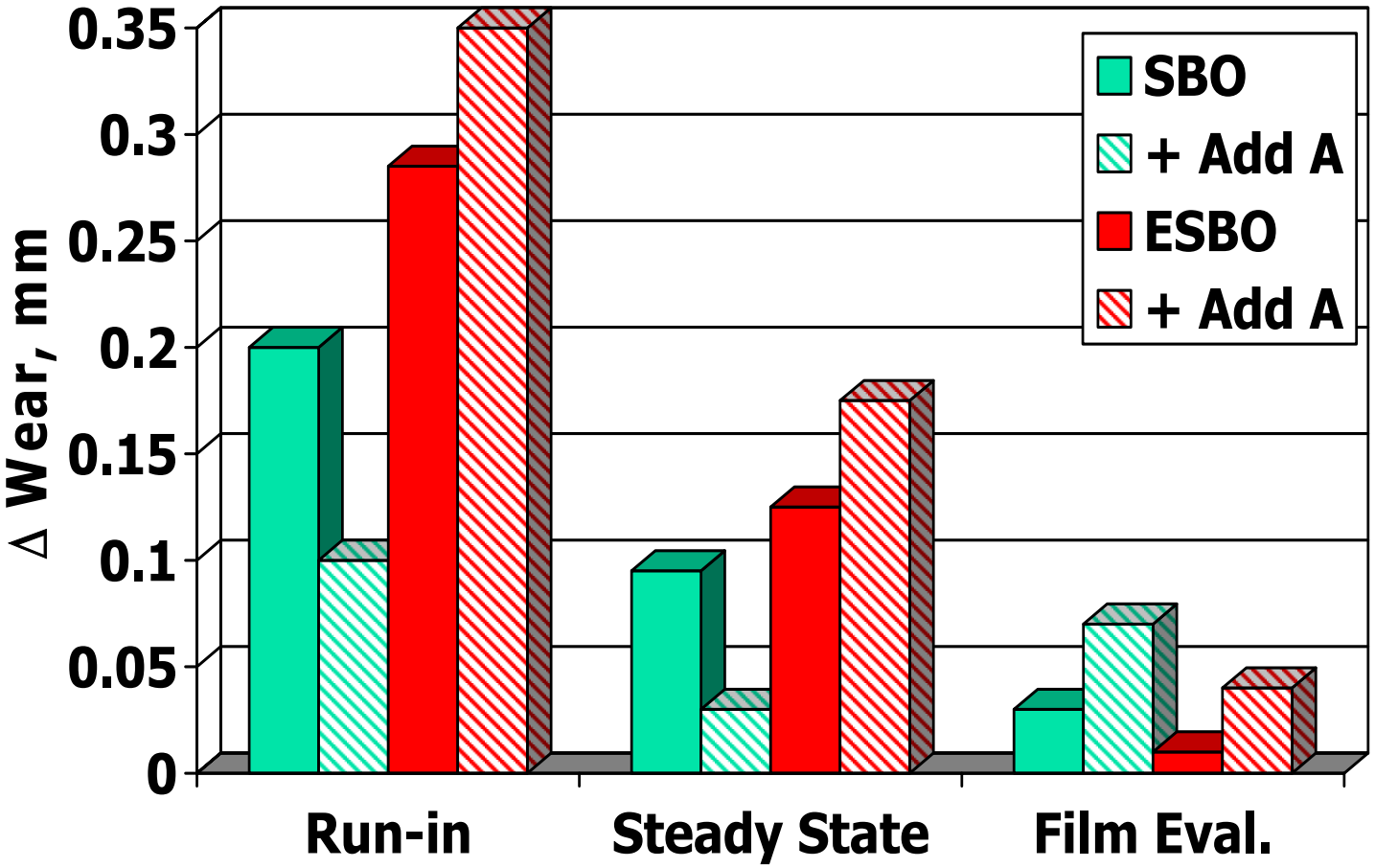
Additive Effectiveness - Additive A



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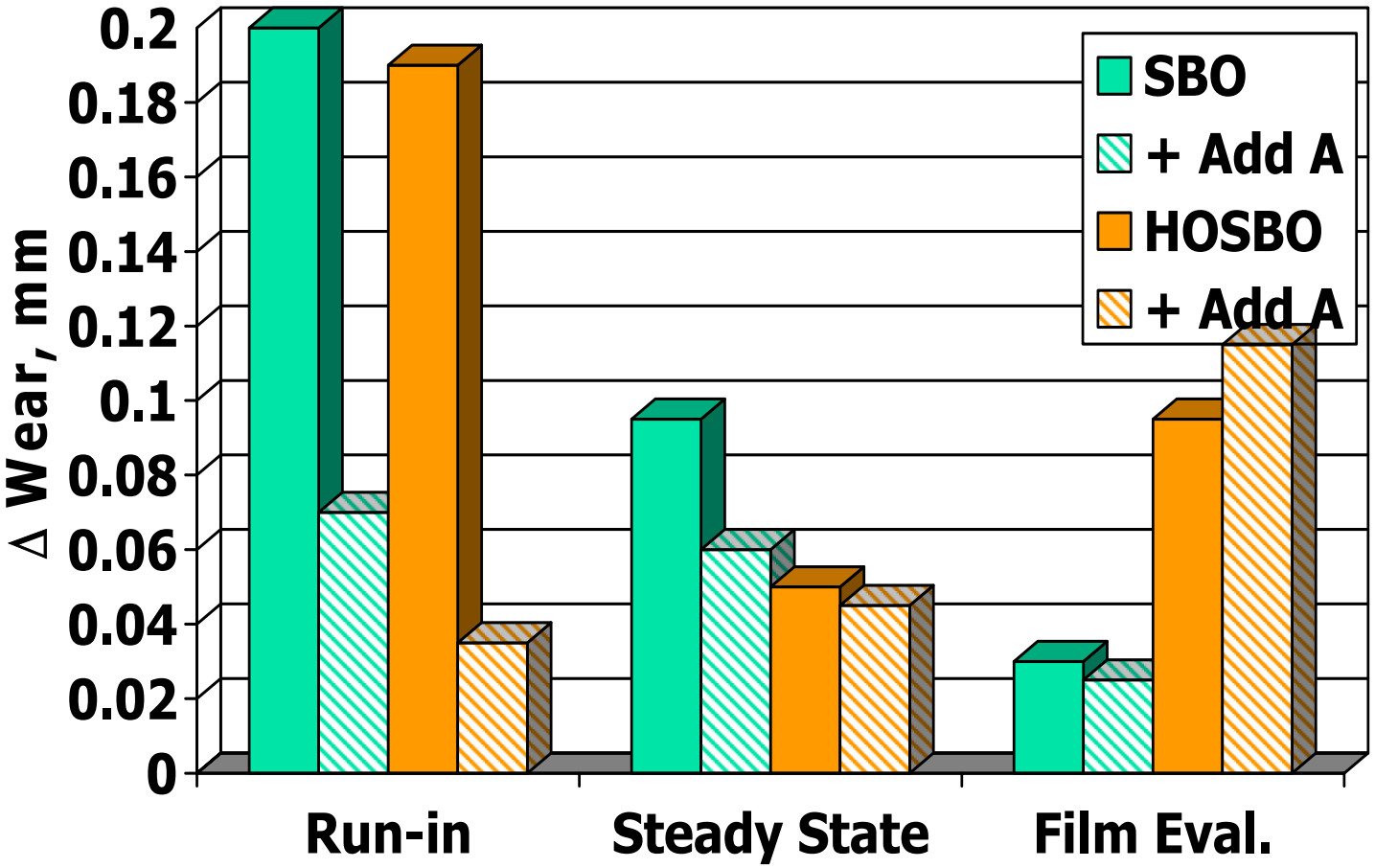
Effect of Unsaturation - Additive A



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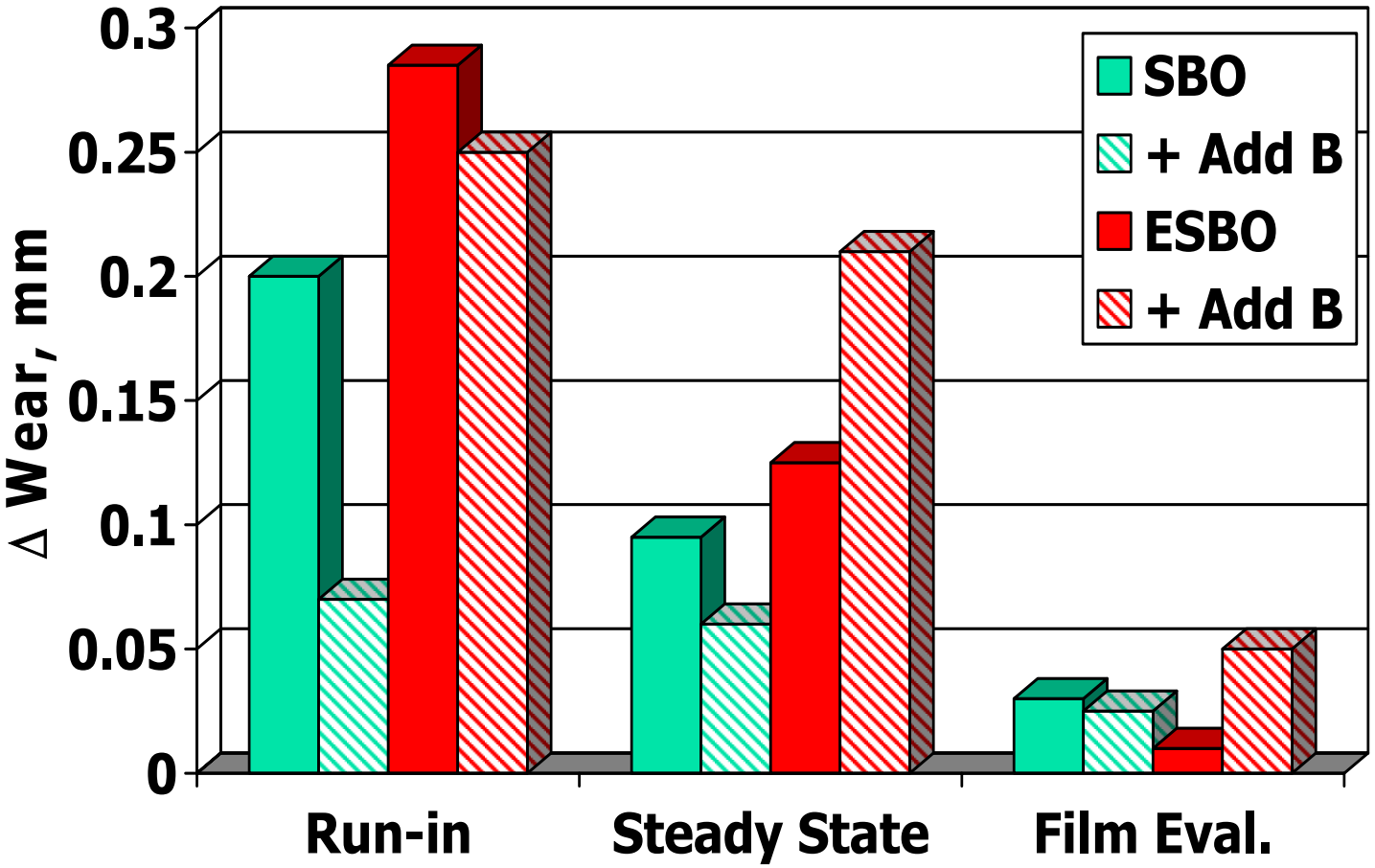
Additive Effectiveness - Additive B



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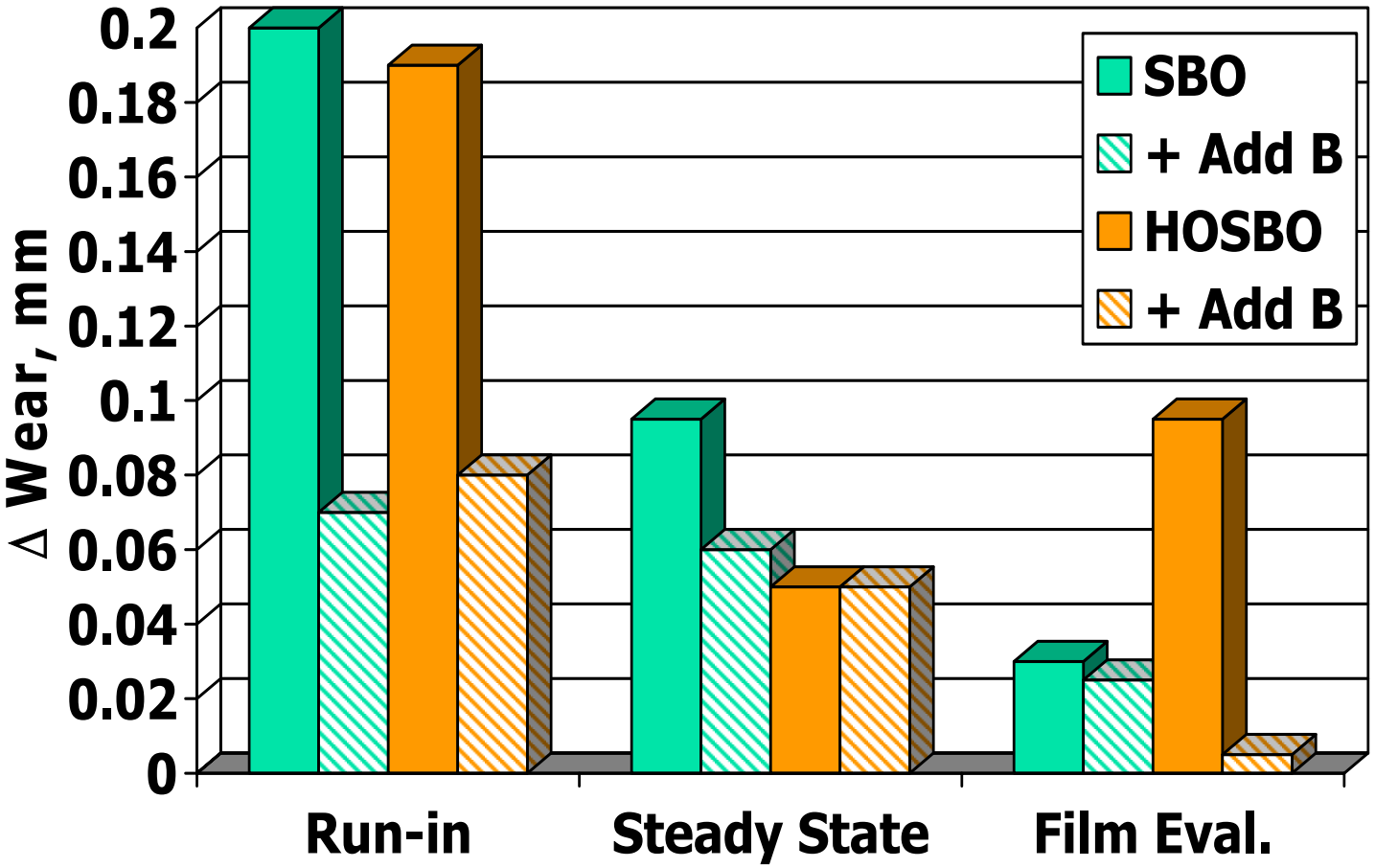
Effect of Unsaturation - Additive B



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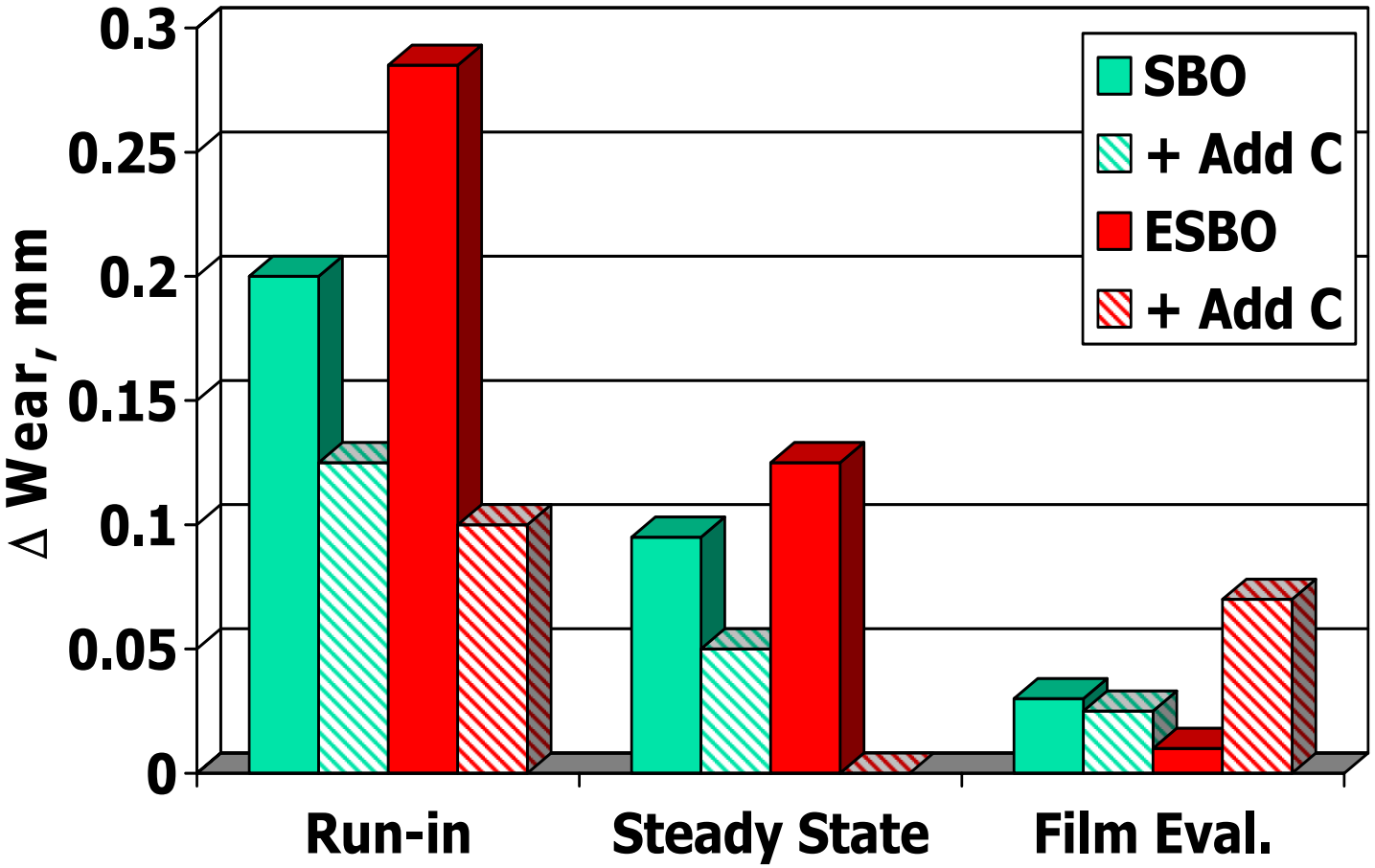
Additive Effectiveness - Additive C



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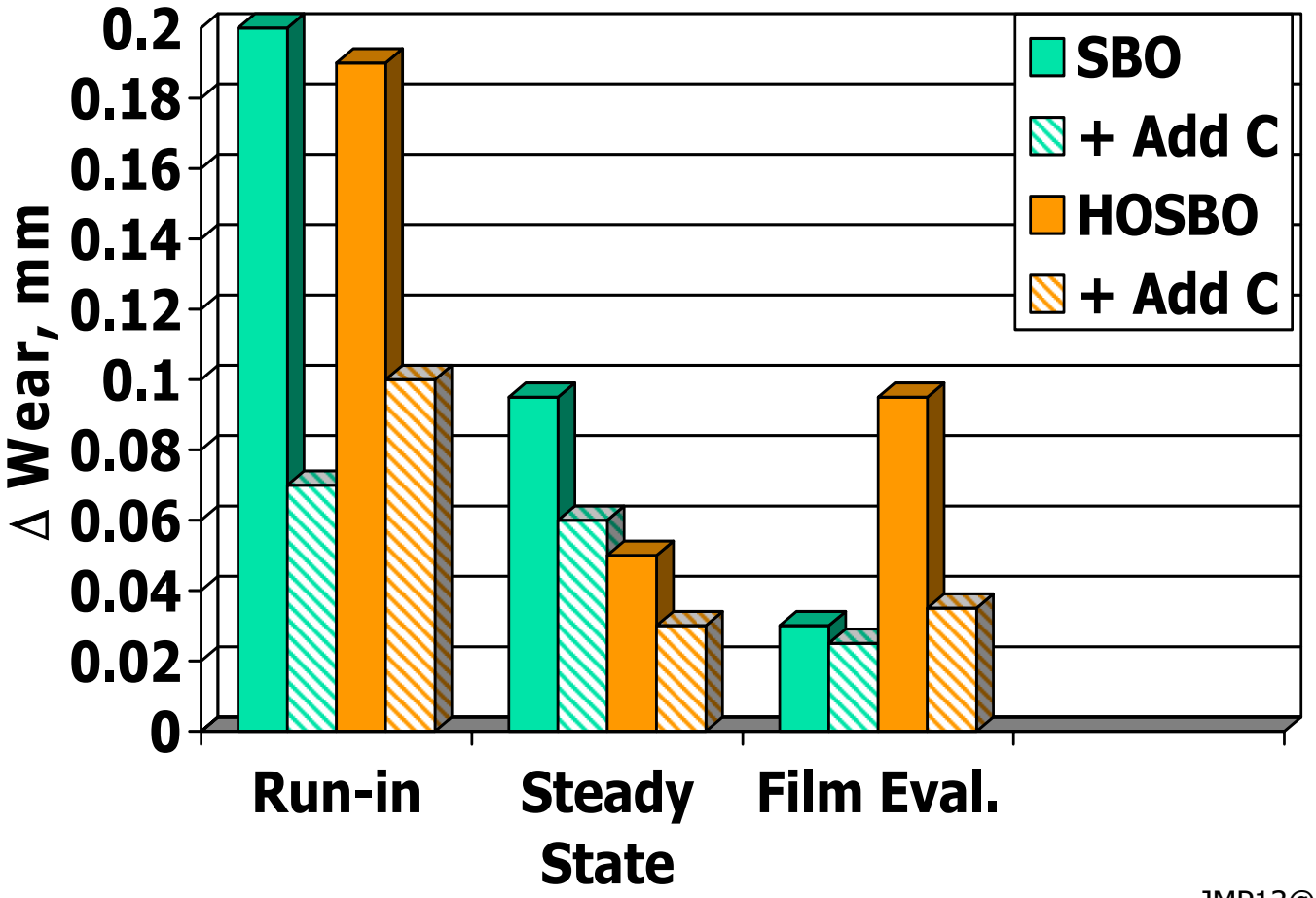
Effect of Unsaturation - Additive C



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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.

Acknowledgement

- Appreciation is given for partial funding of these projects by Air Products; Cargill Corp; Caterpillar, Inc.; Cummins Engine Co.;USDA Laboratory (Peoria, Il) and Valvoline, Inc. Their financial support is appreciated.

- A special thanks to Dr. George Fenske and the Tribology Group at Argonne National Laboratory for their continued interest and support of this research.

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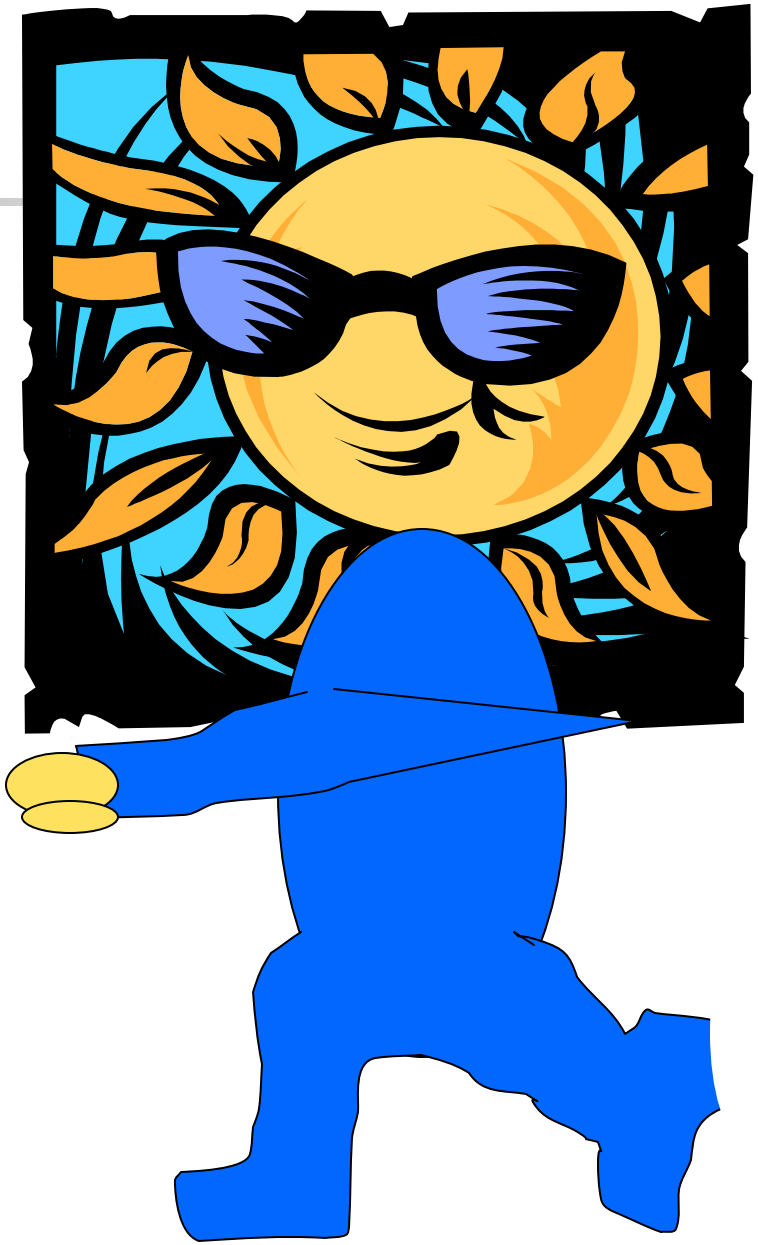
The research contributions of the following Graduate Students is acknowledged:

- Penn State University:
  - Kimberly Wain – Biodiesel Fuels, DME
  - Elana Chapman–DME, Oxygenated Fuels
  - Waleska Castro – Veg. Oils, f & wear tests
  - Kraipat Cheenkachorn – Vegetable Oils
  - David Weller – Chemical Characterization
- Northwestern University:
  - Ashlie Martini - Pin-on-disc studies,
  - Mark Sturino - Pin-on-disc studies, Optical Microscopy

No Not JOEPA



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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]