



Biodiesel Impact on Engine Oil Performance

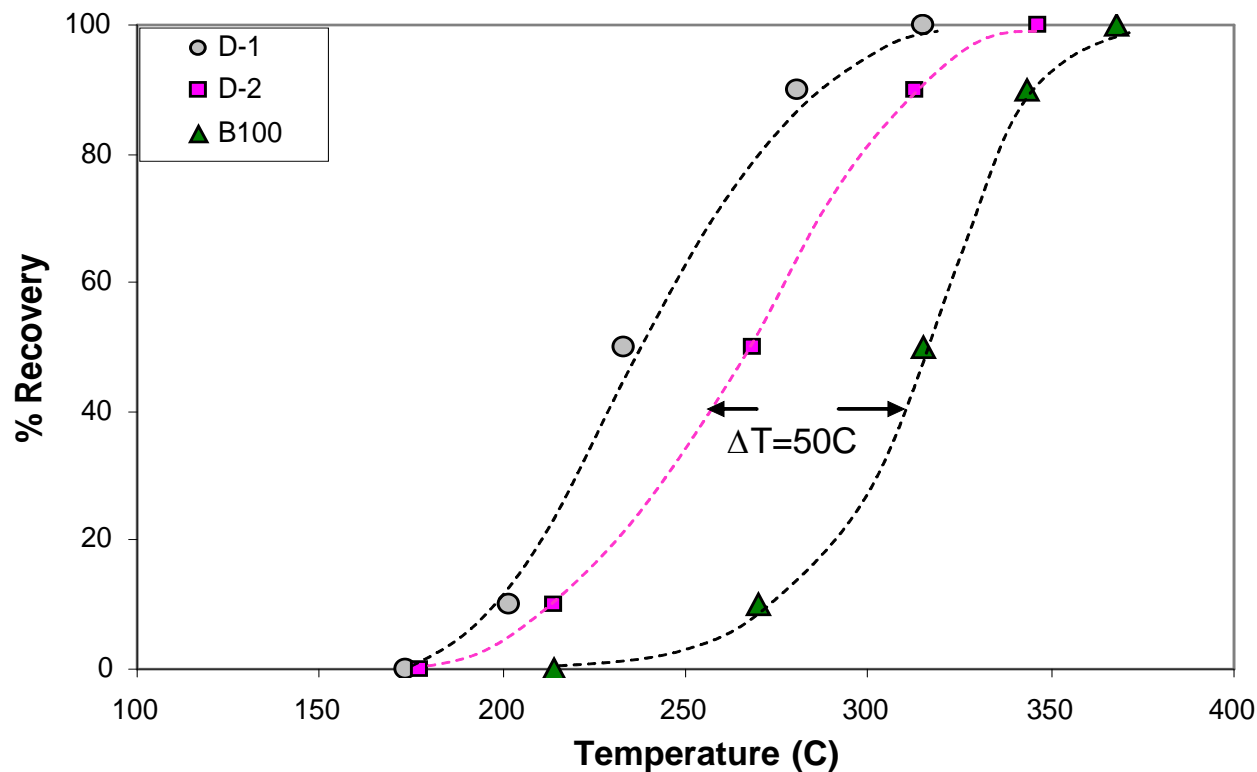
Howard L. Fang, Cummins Inc.

National Biodiesel Conf & Expo
Kissimmee, Florida
Feb. 4, 2008

Biodiesel promotes fuel dilution



- Higher distillation temperature
- Higher surface tension and higher specific gravity
-larger fuel droplet size to condense on cylinder wall
- Lower volatility and higher affinity toward oil additives
-less likely to vaporize from crankcase oil





Adverse biodiesel effects on engine oil

- **Methyl ester and its degradation products may compete with antiwear ZDDP additive towards metal surfaces**
 - Wear/corrosion performance determines the limit for oil drain intervals
 - Wear increase can be related to the film stability of the protection layer
- **Biodiesel promotes fuel dilution in oil particularly with late-injection in aftertreatment regeneration**
 - SAE2006-01-3301 and SAE2007-01-4036
 - High biodiesel dilution carries more water into the oil that may de-stabilize the overbased detergents (Normally 1% fuel dilution will introduce 10 ppm additional water into the oil)
 - Sludge derived from oxidation or interaction with additives can degrade piston cleanliness



Beneficial effects on engine oil

- **Biodiesel and degradation products are potent friction modifiers**

- Biodiesel blends assist fuel lubricity and can minimize the use of lubricity additives

- It needs to be verified

- **Dispersancy improvement by biodiesel soot**

- Dispersancy improvement is caused by different PM morphology using biodiesel fuel where more oxygenates are coupled into the soot structure resulting in a better soot suspension by dispersant

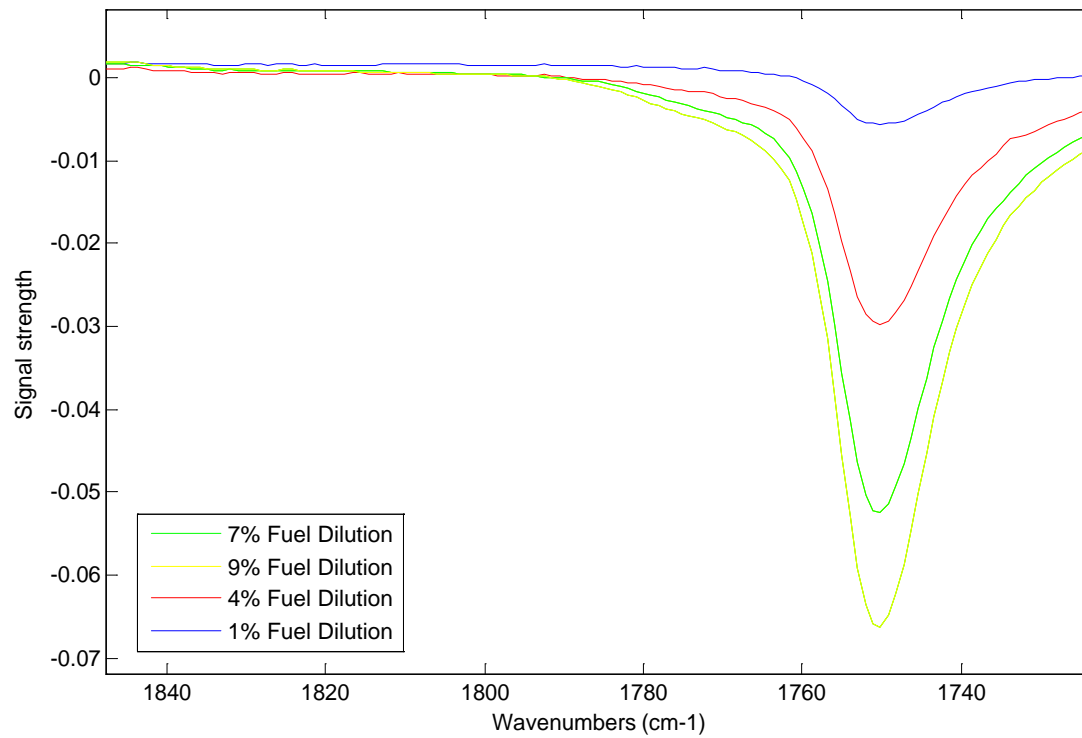
- The dispersancy benefit can be evaluated by viscosity measurement

- It is important to determine the blending threshold for viscosity benefit

Oil tracer approach on fuel dilution



For fuel tracer approach, including IR, GC and isotope labeling, the quantification of fuel dilution (FD) in oil is based on an appropriate calibration with 'known' amount of the biodiesel in engine oil. The unknown FD value is predicted through the slope of such calibration function. However, the exact concentration of biodiesel in the oil on cylinder wall is actually 'unknown' due to low distillation. Oil tracer approach is needed





Sample selection

Sample

Soln-A: 2 % HPE in S150N

Soln-B: 4 % HPE in S150N

Soln-C: 5 % HPE in S150N

Soln-D: 8 % HPE in S150N

Soln-E: 2 % PE in S150N

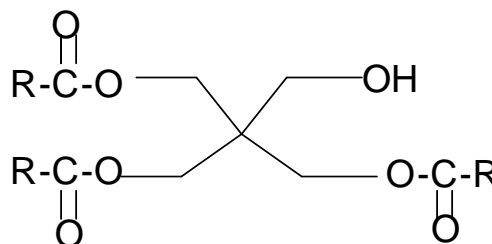
Soln-F: 5 % PE in S150N

Soln-G: 8 % PE in S150N

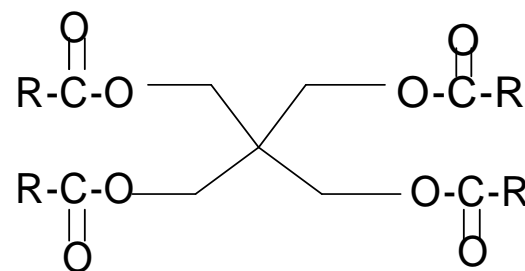
ZDDP: Oloa 262

Baseoil: S150N

Partially esterified pentaerythritol (HPE)
Hydroxy # 60



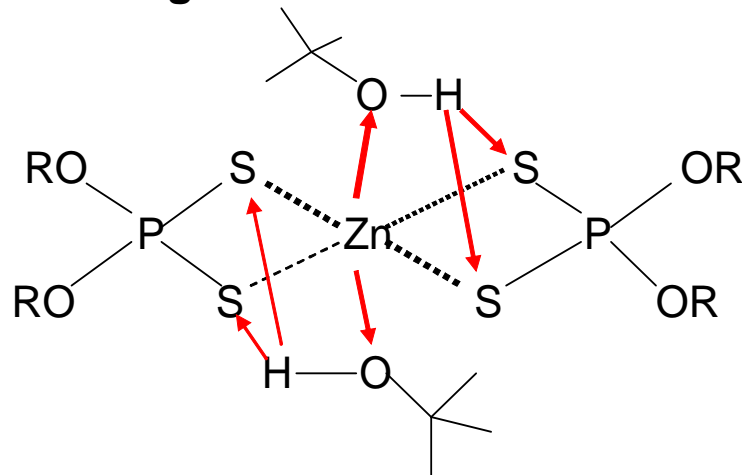
Fully esterified pentaerythritol (PE)





Hydroxy ester interaction with ZDDP

- Both ν_{COP} (974 cm^{-1}) and $\nu_{\text{P=S}}$ (652 cm^{-1}) of ZDDP are sensitive to environment
- Hydroxy ester (partially esterified species) can form complex with ZDDP through hydrogen-bonding



- Under complex formation, the absorption strength of ν_{COP} (974 cm^{-1}) and $\nu_{\text{P=S}}$ (652 cm^{-1}) will be reduced following the hydroxy concentration
- Fully esterified esters should show little interaction with ZDDP

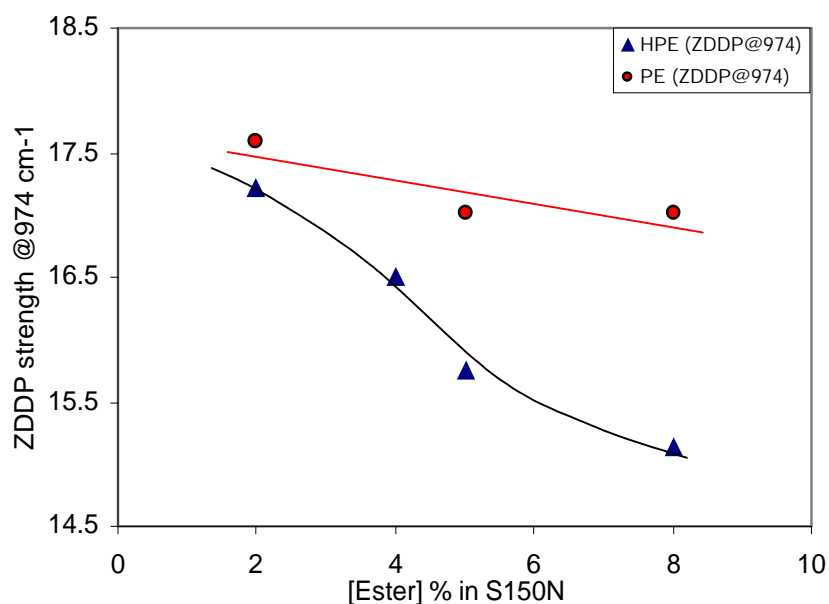
Differential IR data of ZDDP in ester solutions



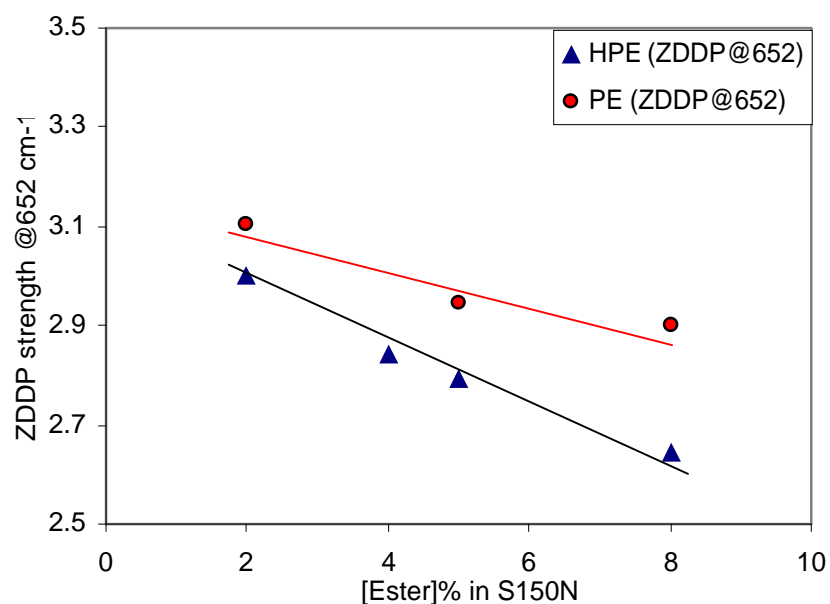
Sample	ZDDP ν_{COP} (1050-910 cm^{-1})	ZDDP $\nu_{\text{P=S}}$ (690-620 cm^{-1})	Ester Carbonyl (1789-1720 cm^{-1})
Soln-A (2% ZDDP in Soln-A) – (Soln-A)	17.221	2.998	10.315
Soln-B (2% ZDDP in Soln-B) – (Soln-B)	16.498	2.841	20.403
Soln-C (2% ZDDP in Soln-C) – (Soln-C)	15.757	2.798	25.758
Soln-D (2% ZDDP in Soln-D) – (Soln-D)	15.138	2.645	41.001
Soln-E (2% ZDDP in Soln-E) – (Soln-E)	17.582	3.149	12.674
Soln-F (2% ZDDP in Soln-F) – (Soln-F)	17.015	2.944	31.889
Soln-G (2% ZDDP in Soln-G) – (Soln-G)	17.008	2.901	52.196



ZDDP decay rates are faster in hydroxy ester (HPE) than in full ester (PE)



At 8% concentration, the ν_{COP} band drop is 12 % for HPE and only 3 % for PE



At 8 % concentration, the $\nu_{\text{P=S}}$ band drop is 12 % for HPE and only 2% for PE

³¹P NMR data

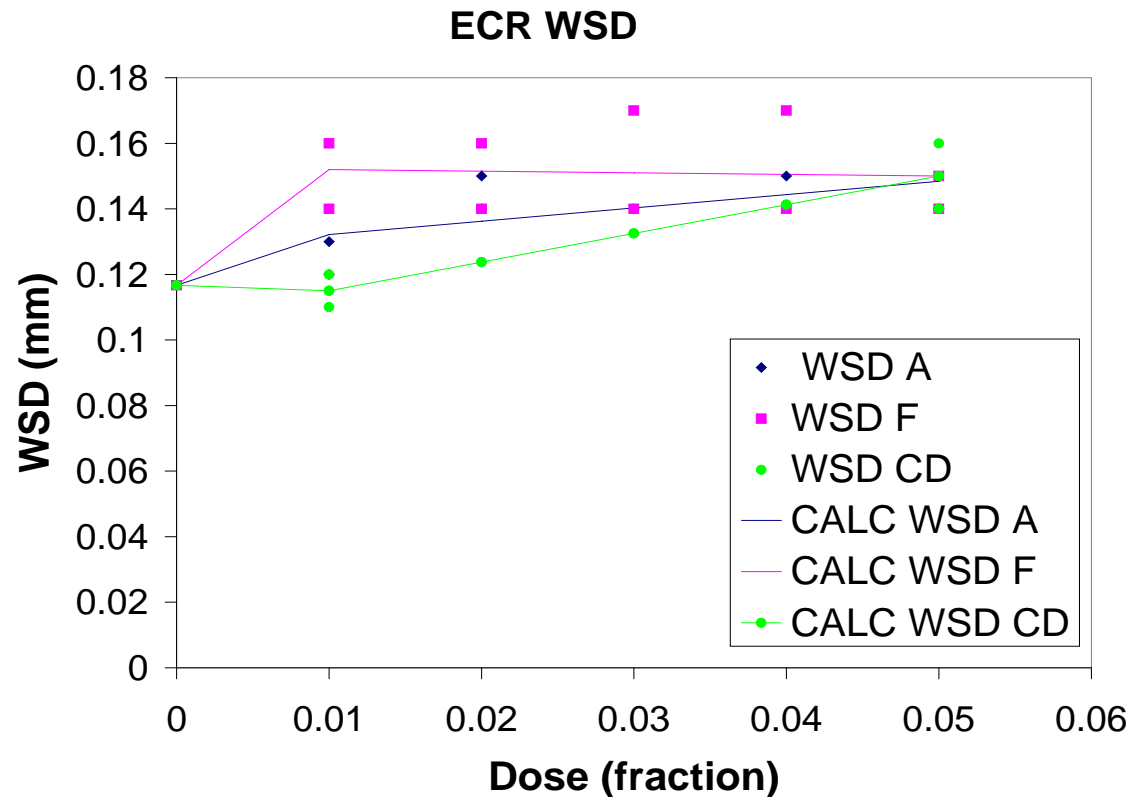


Sample	2°-ZDDP		1°-ZDDP	
	Basic	Neutral	Basic	Neutral
1% ZDDP in PAO as is and @70°C	100.6 (14.2%)	94.5 (61.6%)	102.5 (12.8)	96.4 (11.6%)
1% ZDDP in a mixture of 10% HPE/PAO @25°C	100.5 (12.7%)	94.4 (57.5%)	102.5 (16.8)	96.4 (13%)
1% ZDDP in a mixture of 10% HPE/PAO @50°C	100.5 (9.9%)	94.3 (58.2%)	102.5 (17.5)	96.4 (14.4%)
1% ZDDP in a mixture of 10% HPE/PAO @70°C	100.4 (7.4%)	94.1 (65.3%)	102.5 (11.5%)	96.2 (15.8%)
1% ZDDP in a mixture 10% HPE/PAO @90°C	100.3 (4%)	94.0 (63%)	*	96.1 (16%)

*: area not integratable



Electric Contact Resistance (ECR) data



A: aged biodiesel

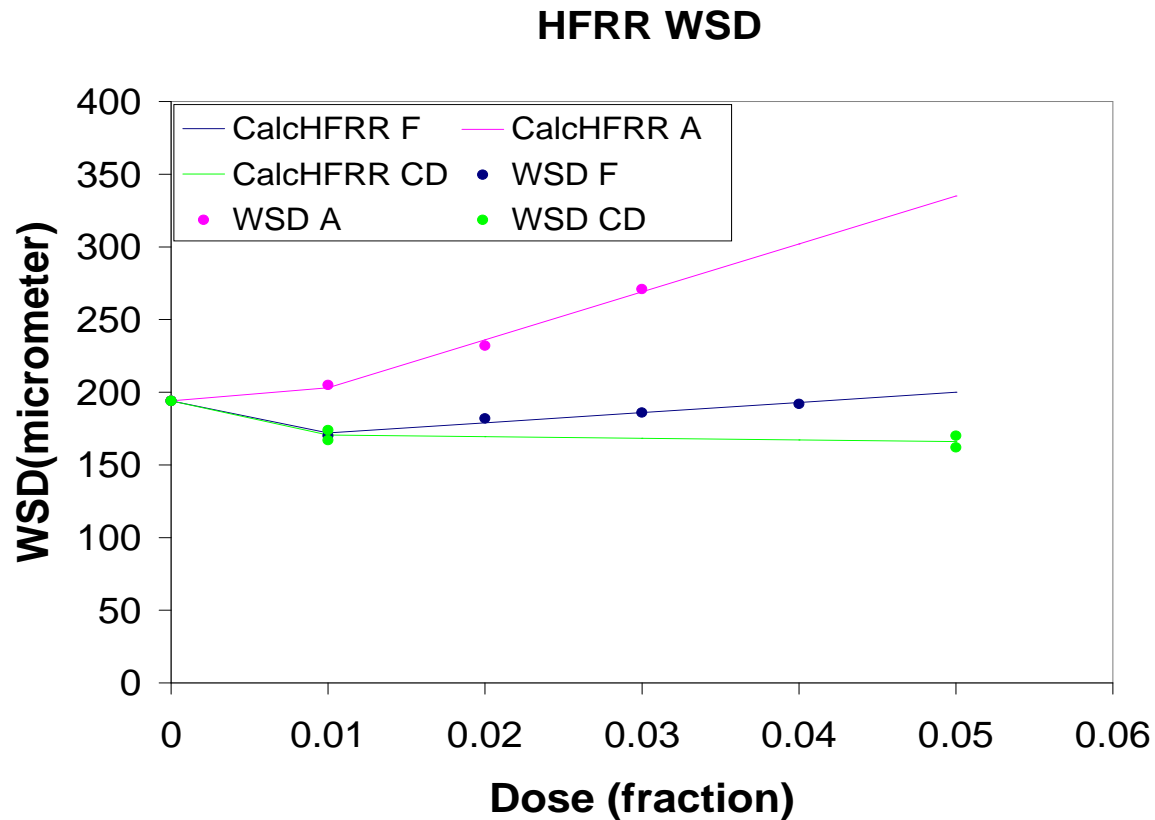
F: fresh biodiesel

CD: certified ULSD

Biodiesel aging was conducted by heating @110C for 20 hr under air flow



High Frequency Reciprocating Rig (HFRR) data

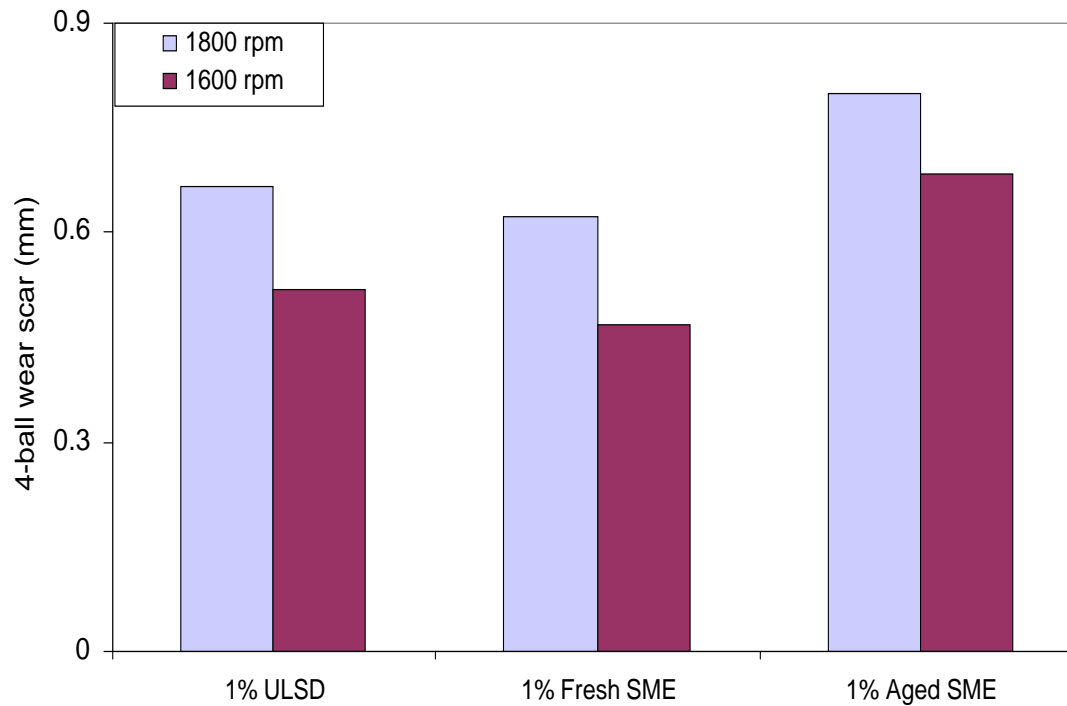


A: aged biodiesel

F: fresh biodiesel

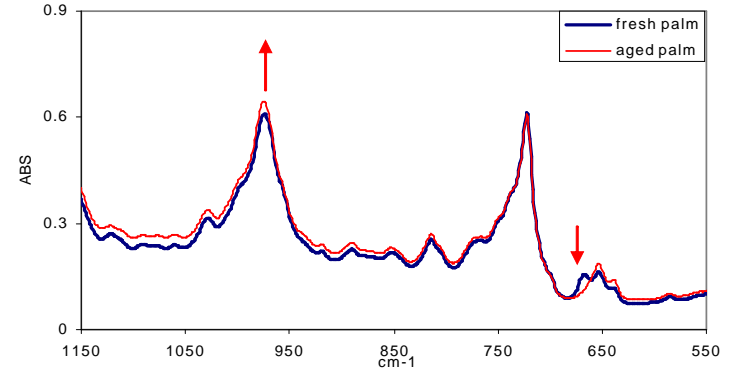
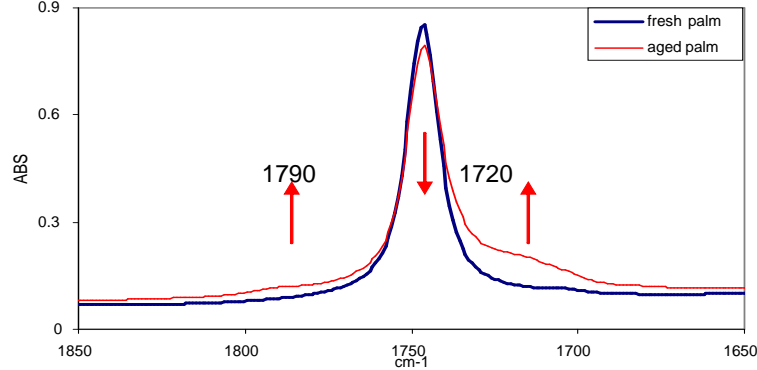
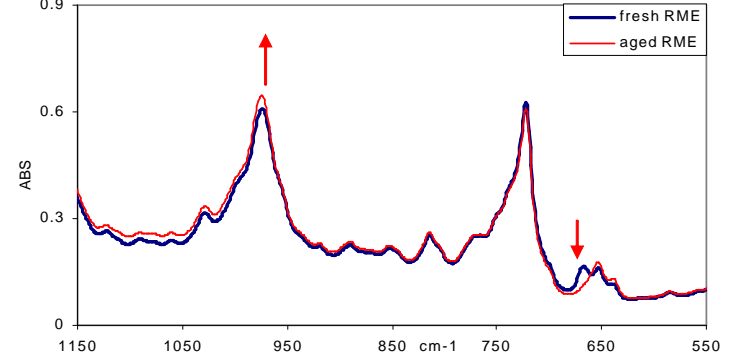
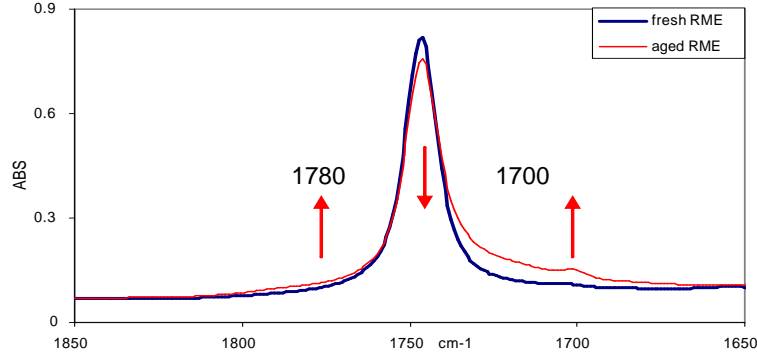
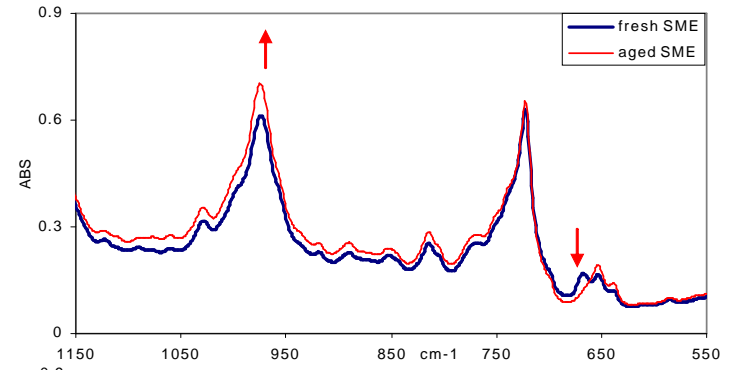
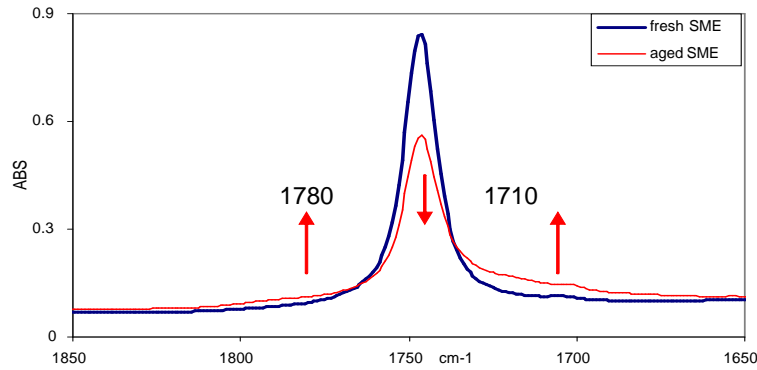
CD: certified ULSD

Four-ball wear test data



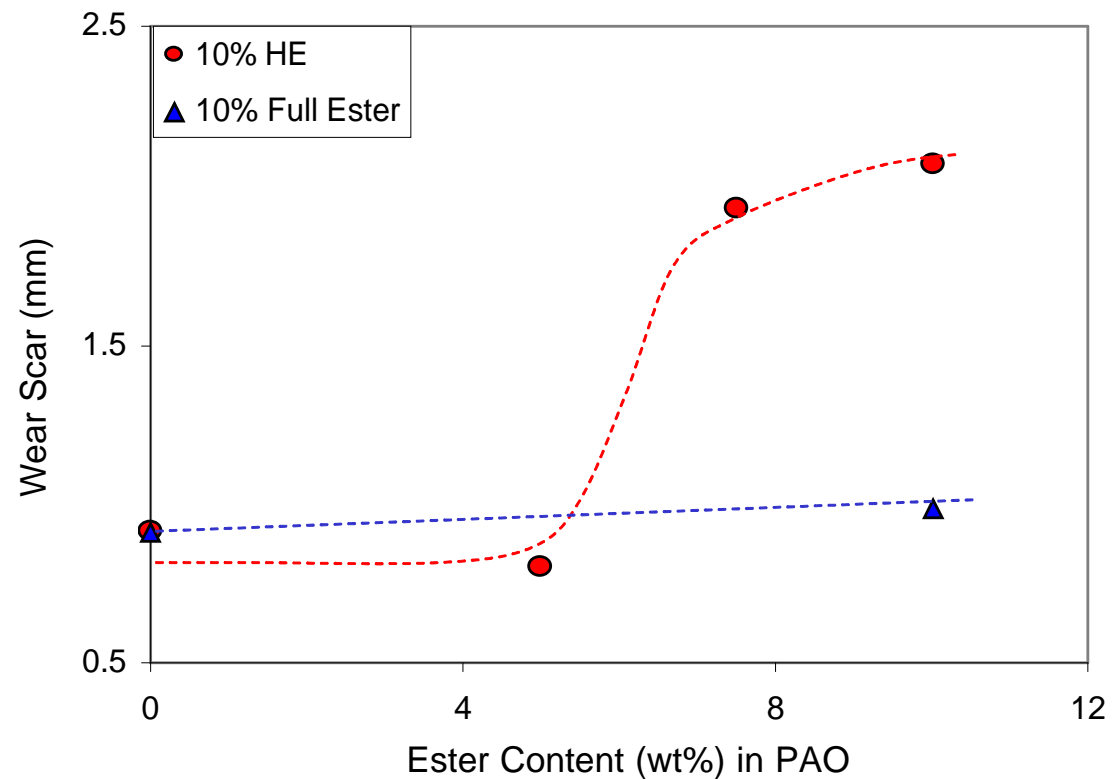
40 kg load, 60 minute period, 120°C with 1600 and 1800 rpm speed

IR data of interaction between aged biodiesel and ZDDP

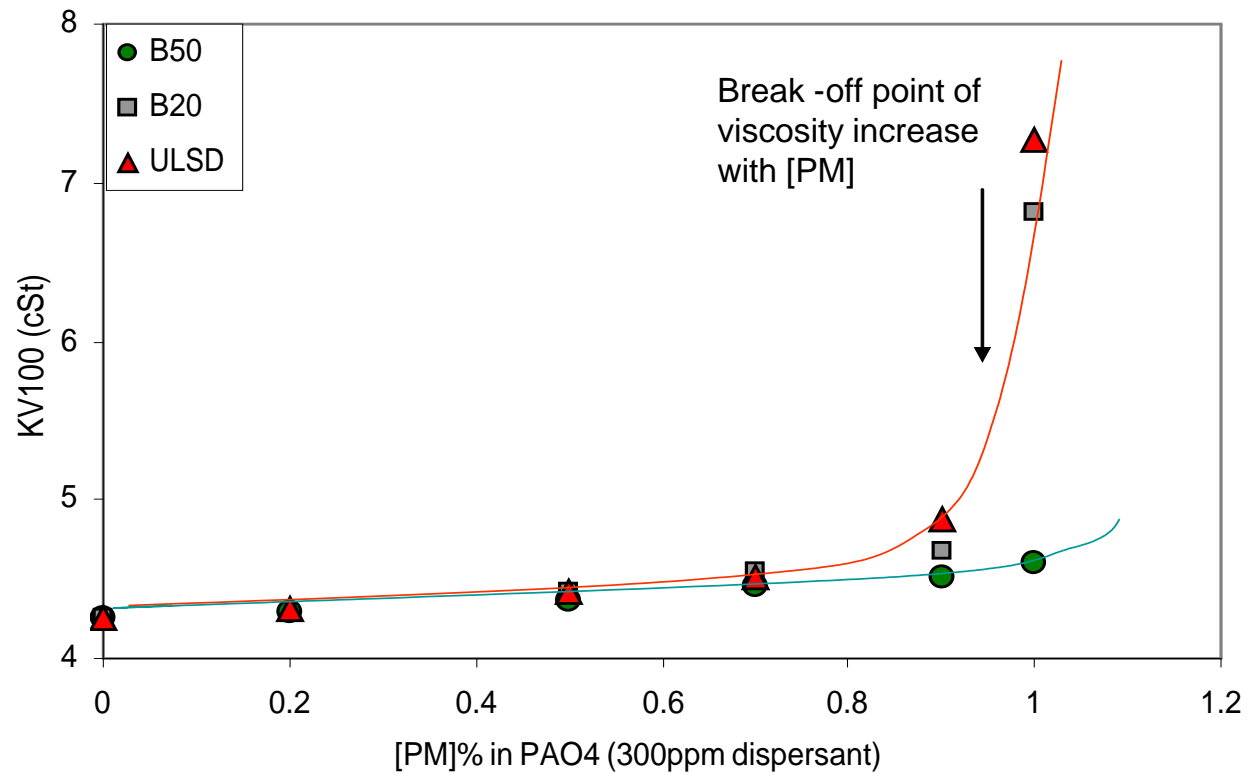




Concentration dependence of wear scar on hydroxy ester as evaluated by four-ball



Dispersancy evaluation by KV100



Dispersant: PIBSA/PAM (MW=5000m, 300 ppm in PAO4)

Conclusions



- **Oil dilution by aged biodiesel may increase engine wear even at concentration of 5% or less**
- **Excessive fuel dilution of biodiesel can lead to complex formation between oxidized biodiesel species and ZDDP**
 - Even under different tribological conditions, HFRR and four-ball give similar results for oil containing aged biodiesel
- **Aged biodiesel causes wear increase while fresh biodiesel might actually decrease wear**
- **B50 seems to be the limit for soot suspension benefit when a level of 300 ppm dispersant is used in PAO4**