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# Impact of Biodiesel on Ash Emissions and Lubricant Properties Affecting Fuel Economy and Engine Wear

## *Comparison with Conventional Diesel Fuel*

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Alexander G. Sappok and Victor W. Wong

**Massachusetts Institute of Technology**

**Sloan Automotive Laboratory**


DETROIT MICHIGAN 2007 DIESEL ENGINE-EFFICIENCY & EMISSIONS RESEARCH CONFERENCE

# Motivation

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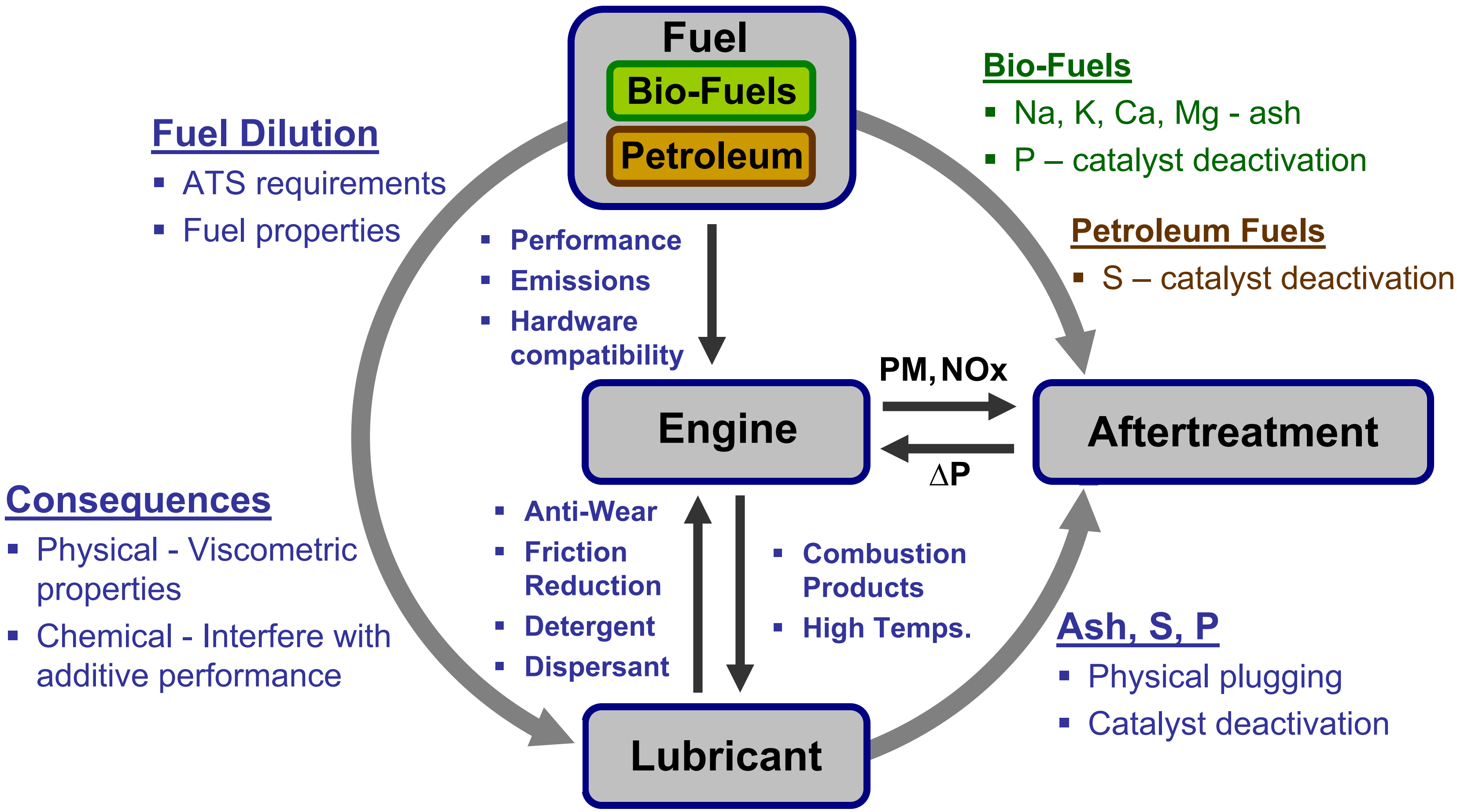
**Fuel and lubricant composition affects engine and aftertreatment system (ATS) performance.**




*Effect of bio-fuel on lubricant properties via fuel dilution and ATS performance via PM and ash emissions not well known.*

# Background

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- **Bio-fuel effects on aftertreatment system (ATS) performance**
  - Potential for residual alkali and alkaline earth metals to form ash
    - ASTM D6751 – 5 ppm limits for Na and K, Ca and Mg
    - **1 $ppm_w$** trace metal in fuel **~ 22 g trace metal** in DPF per 100k miles assuming 15 mpg and 100% trapping efficiency
  - Decreased PM emissions
    - Reduce frequency of regeneration
    - Bio-diesel generated PM may oxidize more rapidly

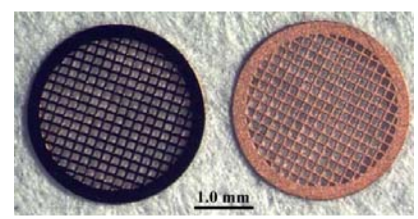
- **Bio-fuel effects on lubricant properties**
  - Distillation characteristics and boiling range affect amount of fuel reaches cylinder walls*
  - Initial decrease followed by increase in lubricant viscosity due to oxidation and polymerization of fuel constituents (SAE 2005-26-356)
  - Polar nature of methyl esters may react with P in ZDDP to form complexes preventing anti-wear additives from coating surfaces (SAE 2006-01-3301)
  - Polar species may destabilize over-based detergents (SAE 2003-01-3140)

# Experimental Apparatus



- **Cummins ISB 300**
  - Variable geometry turbocharger
  - Cooled EGR
  - Common rail fuel injection
  - Fully electronically controlled
- **PM Sampling**
  - Conventional 47 mm filters
  - Individual particulate collection using 3mm dia. TEM grids
- **Sample Analysis**
  - Horiba MEXA 1370 – SOL, SOF, $SO_4$
  - TGA – Total ash content
  - Scanning Transmission Electron Microscopy (STEM)
    - PM and ash morphology and elemental composition

**2002 Cummins ISB 300**


Comparison of conventional 47mm filters and 3mm sample grids

# Accelerated Fuel Dilution System

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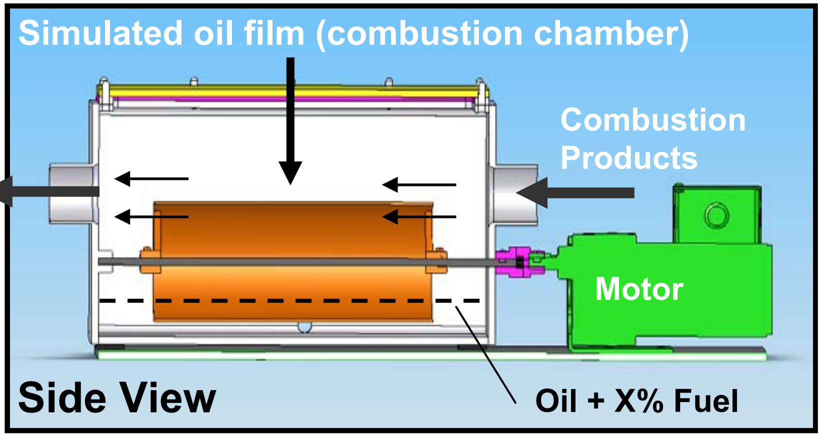
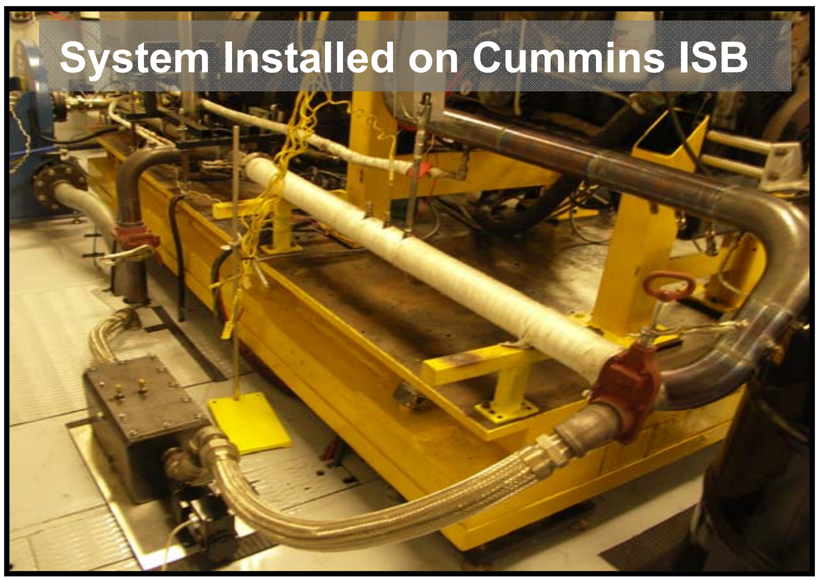
**Objective:** Simulate fuel dilution and accelerate lubricant aging under controlled conditions.




## Key Parameters

**Temperature:** 165 °C sump, 220 °C inlet

**Volume:** 1 L lubricant (6 L max.)

**Speed:** 5.5 rpm (30 max.)

**Duration:** 12 hrs steady state

- **Test Matrix**
  - CI-4, CJ-4 oil
  - No dilution
  - 5% ULSD, 5% SME B100
- **Test Sequence**
  1. Rapid aging system: 12 hours
  2. Bench oxidation: 78 hours
- **Lubricant Analysis**
  - TAN, TBN, Viscosity, FTIR, ICP
  - 4-Ball Wear

# Lubricant Composition – 15W-40

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## Lubricant Elemental Analysis

| Lubricant Condition | B | Ca | Fe | Mg | Mo | P | Zn | S |
|---|---|---|---|---|---|---|---|---|
| | ASTM D5185 | | | | | | | |
| | [ppm] | [ppm] | [ppm] | [ppm] | [ppm] | [ppm] | [ppm] | [ppm] |
| **Fresh CI-4** | <1 | 2352 | 2 | 269 | 1 | 1181 | 1398 | 5863 |
| **Fresh CJ-4** | 586 | 1388 | 2 | 355 | 77 | 985 | 1226 | 4606 |
| **Engine Aged CI-4** | 18 | 2626 | 20 | 267 | 11 | 1246 | 1464 | 6076 |

*Lubricant run in engine for approximately 220 hours at time of sampling*

## Lubricant Properties

| Lubricant Condition | ASTM D3524 | FTIR | | ASTM D445 | ASTM D664 | ASTM D2896 | ASTM D4739 |
|---|---|---|---|---|---|---|---|
| | **Fuel** | **Soot** | **Water** | **Visc. @100 C** | **TAN** | **TBN** | **TBN** |
| | [% Wt] | [% Wt] | [% Vol] | [$mm^2/s$] | [mg KOH/g] | [mg KOH/g] | [mg KOH/g] |
| **Fresh CI-4** | <0.1% | <0.1% | <0.1% | 14.93 | 1.86 | 9.9 | --- |
| **Fresh CJ-4** | <0.1% | <0.1% | <0.1% | 15.8 | 1.74 | 9.6* | 6.66 |
| **Engine Aged CI-4** | <0.1% | 0.10% | <0.1% | 13.13 | 2.17 | 10.42 | --- |

* Supplied by manufacturer

*New and engine aged lubricant provide reference for comparison to accelerated test results*

# Fuel Properties and Hardware Compatibility

| Element | ASTM D5185 | | | | |
|---|---|---|---|---|---|
| | Lowest Reporting Value | B100 Batch 1 | B100 Used | B100 Batch 2 | ULSD |
| | [ppb] | [ppb] | [ppb] | [ppb] | [ppb] |
| Calcium, Ca | 97 | 410 | 198 | 140 | <97 |
| Magnesium, Mg | 56 | <56 | <56 | <56 | <56 |
| Phosphorus, P | 1,180 | <1180 | **2981** | <1180 | <1180 |
| Sodium, Na | 2,010 | <2010 | **22587** | <2010 | <2010 |
| Potassium, K | 2,690 | <2690 | <2690 | <2690 | <2690 |
| Zinc, Zn | 155 | <155 | <155 | <155 | <155 |

**Trace element levels in commercial B100 SME**

| | ASTM D664 | ASTM D3828 | ASTM D6304 | EN 14112 |
|---|---|---|---|---|
| | Acid Number | Flash Point* | Water | Rancimat |
| | [mg KOH/g] | [ °C] | [ppm] | [hr] |
| B100 - Batch 1 | 0.23 | >130 | 314 | 0.56 |
| B100 - Used | **3.36** | <130 | 499 | >12 |
| ASTM D6751 | 0.5 max | 130 min | 500 max | >3 |

**Fuel properties variation for B100 SME**

Injector failure after short duration use with low quality B100 shown in tables as (B100-Used)


Clean Injector


Fouled Injector

# B100 Reduces PM Emissions

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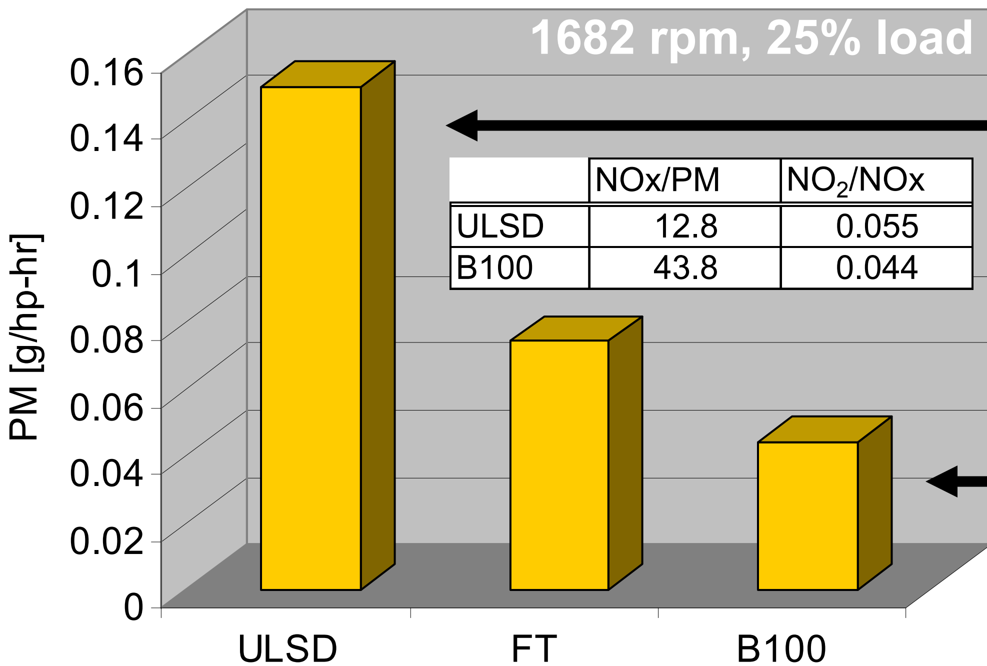
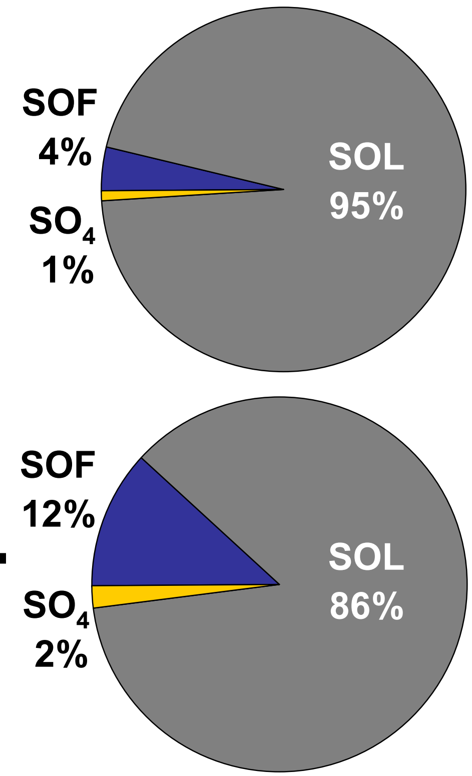
**PM Reduction with B100 SME**




| | NOx/PM | $NO_2$/NOx |
|---|---|---|
| ULSD | 12.8 | 0.055 |
| B100 | 43.8 | 0.044 |




**B100 SME shows 70% reduction in PM**

- Increase in NOx/PM ratio ~ 3X
- Reduced soot loading of engine lubricant
- Aside from soot no additional differences in B100 combustion products observed to affect lubricant

| Total soot in lubricant | Soot [% Wt] |
|---|---|
| **New Oil: CI-4** | <0.1% |
| Engine Aged ULSD | 0.10% |
| Rapid Aged ULSD | 0.10% |
| Rapid Aged B100 | <0.1% |

# Potential for Increased Ash and Faster PM Oxidation

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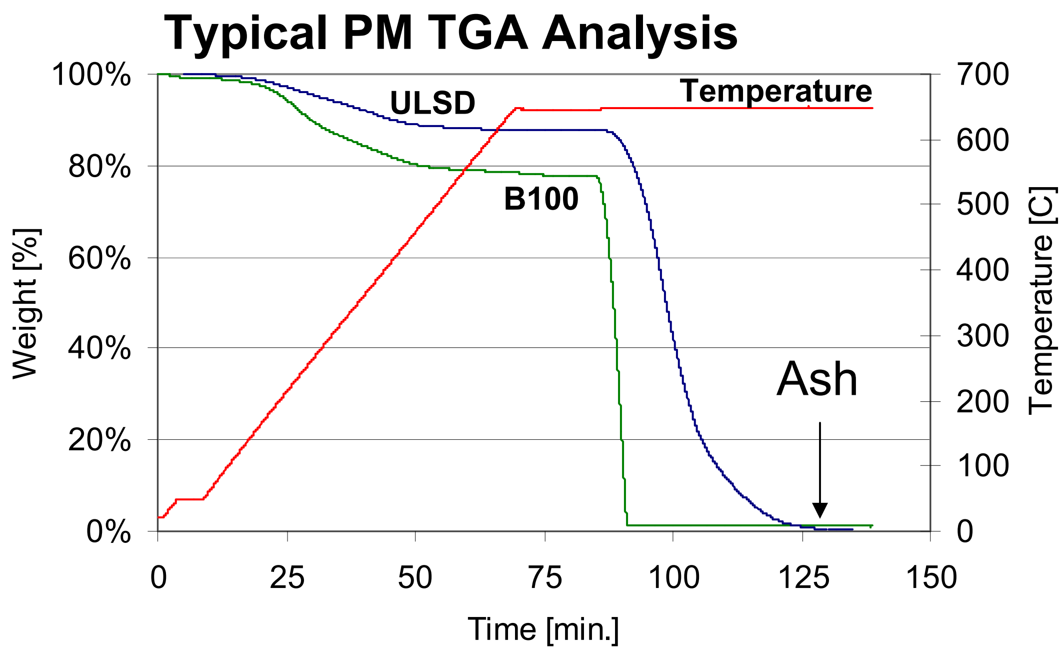


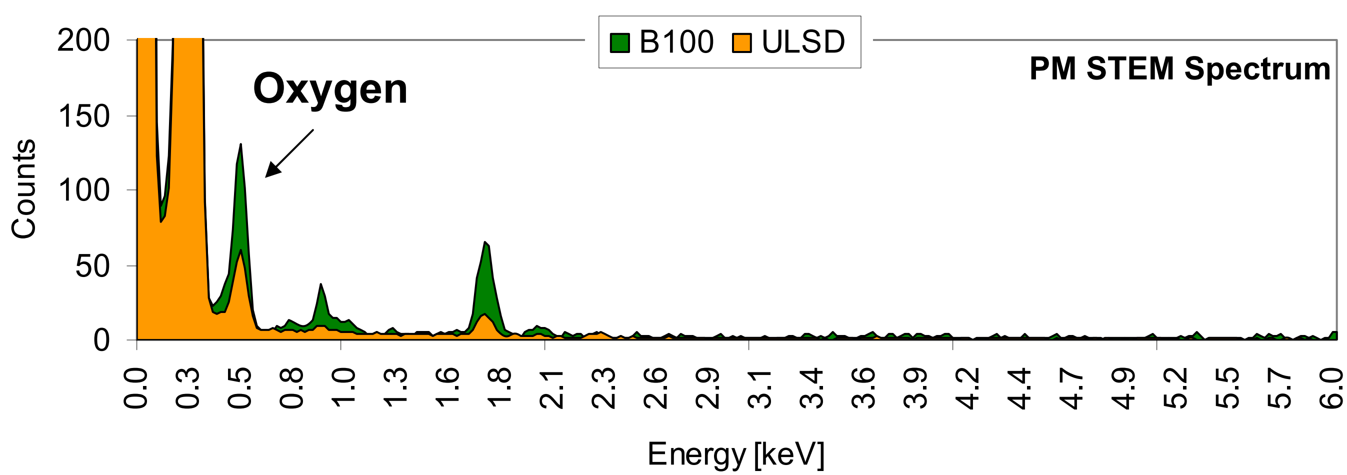

## Ash Fraction

- 1682 rpm, 25% load
- B100: 1.85% of TPM
- ULSD: 0.44% of TPM

## Adjusted Ash Emissions

- Account for PM reduction
- Net Increase in ash with B100 approx. **21.7%**

Biodiesel PM contains more $O_2$ - may increase soot oxidation rate



# Biodiesel Ash Shows Increased Debris and Metals

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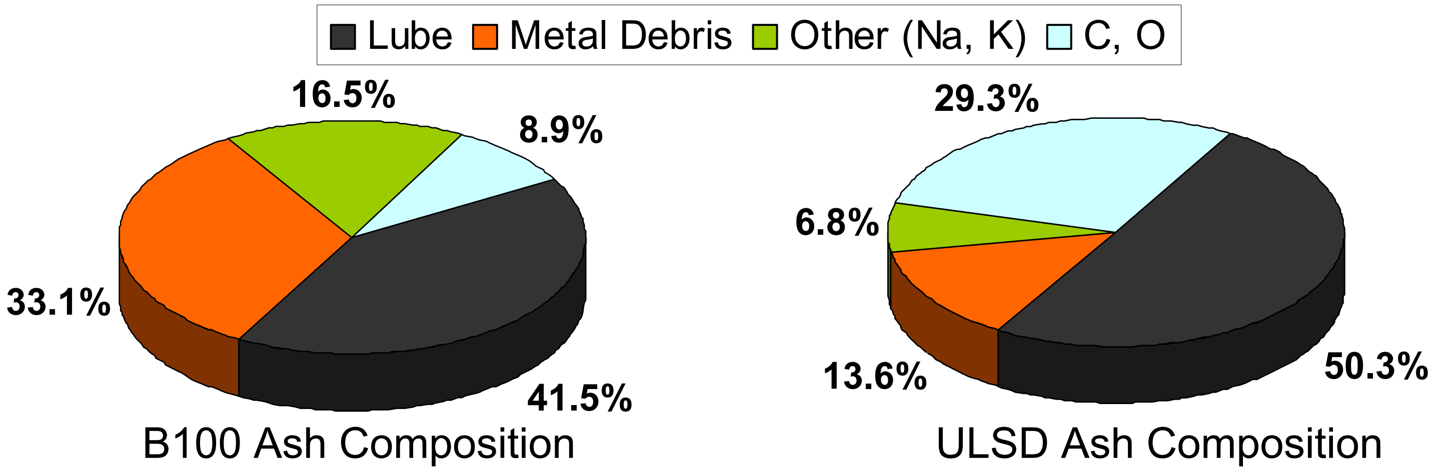


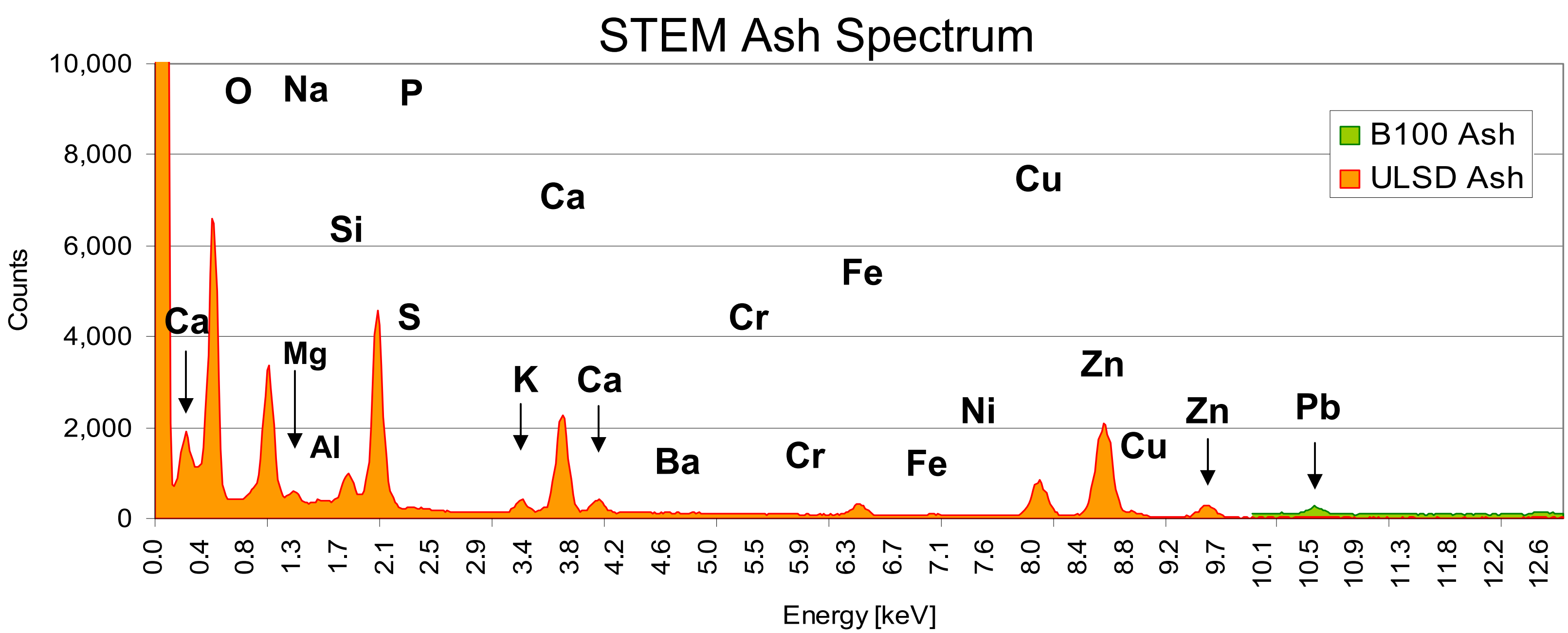


Elevated levels of trace metals in biodiesel ash possibly due to solvent properties of fuel

# Debris and Wear Metal Particles in PM

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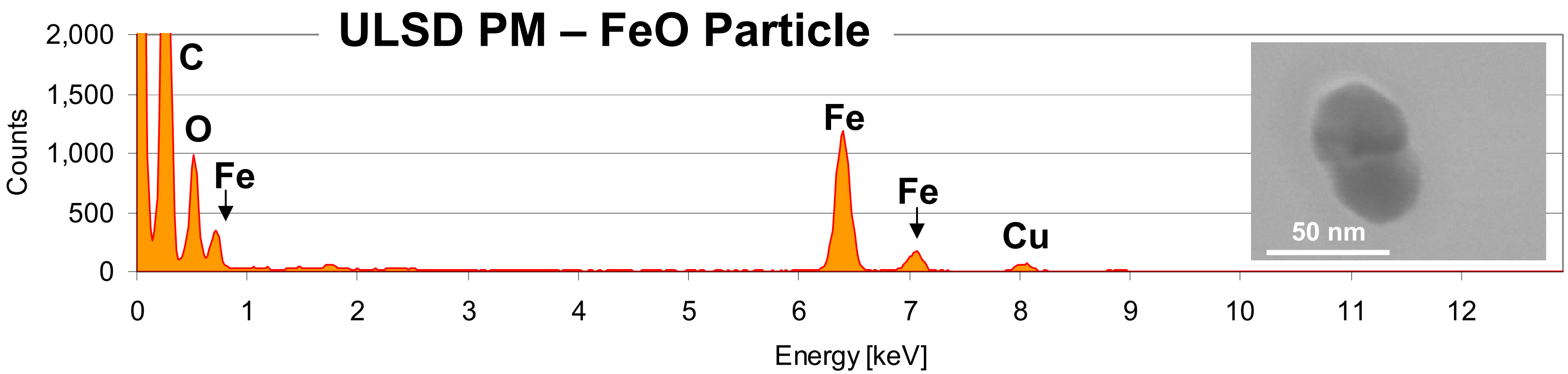
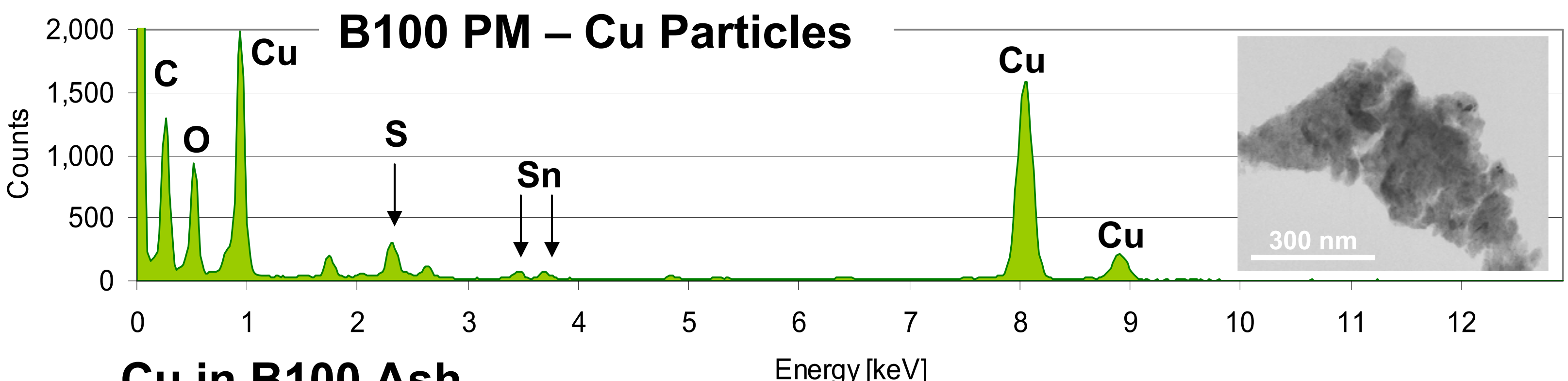
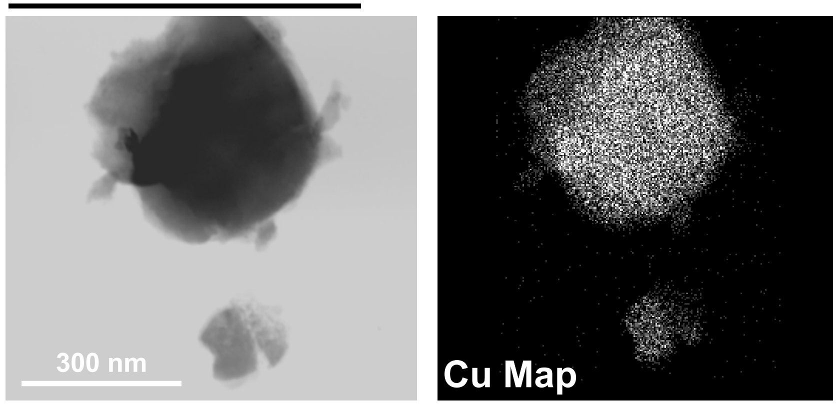



**Cu in B100 Ash**




- Elevated levels of Cu and trace metals found in B100 PM
- Cu particles observed in B100 ash as well
- Only trace amounts of Fe typically observed in ULSD PM

# Fuel Dilution Effects on Lubricant Properties

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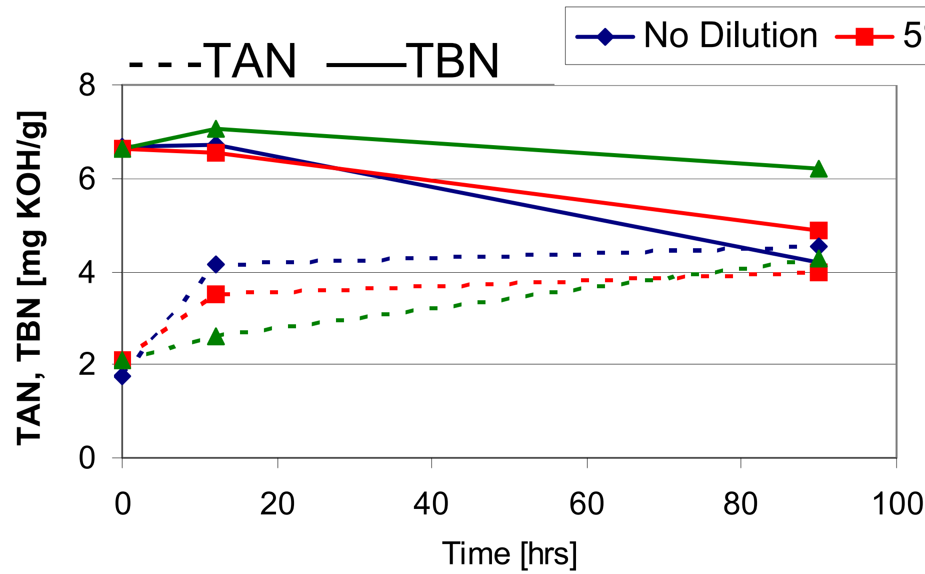
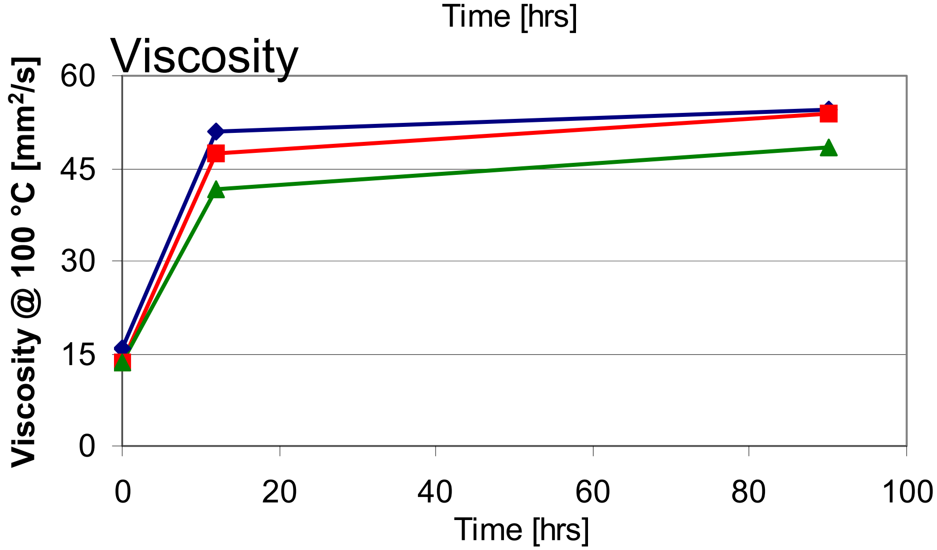
| | | |
|---|---|---|
| CJ-4 Oil | Test: 12 hr rapid aged | Condition: 165 °C sump, 220 °C inlet |
| | Test: 78 hr bench oxidation | Condition: 170 °C, 13 L/h air |




**TBN ASTM D4739, TAN ASTM D664**

- Fuel dilution at 5% shows reduced TBN decline and TAN increase
- Biodiesel most significant effect on reducing TAN and TBN change

**Viscosity ASTM D445**

- Viscosity trends follow observed TAN increase
- Effect of 12 hr rapid aging system on viscosity and TAN increase most significant

# FTIR Biodiesel Fuel Dilution

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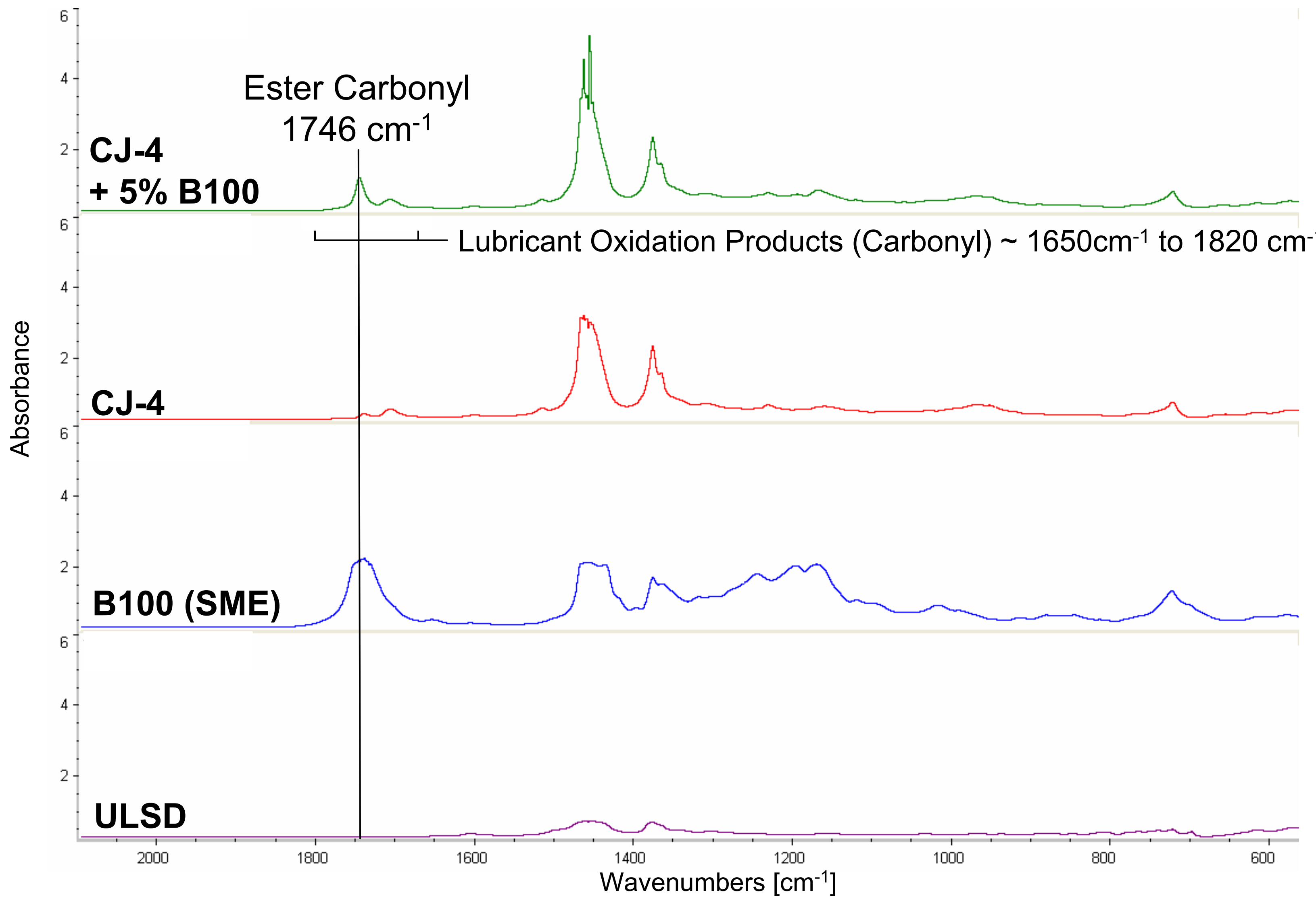


Biodiesel ester peak can interfere with lubricant oxidation measurements

# Oxidation Characteristics

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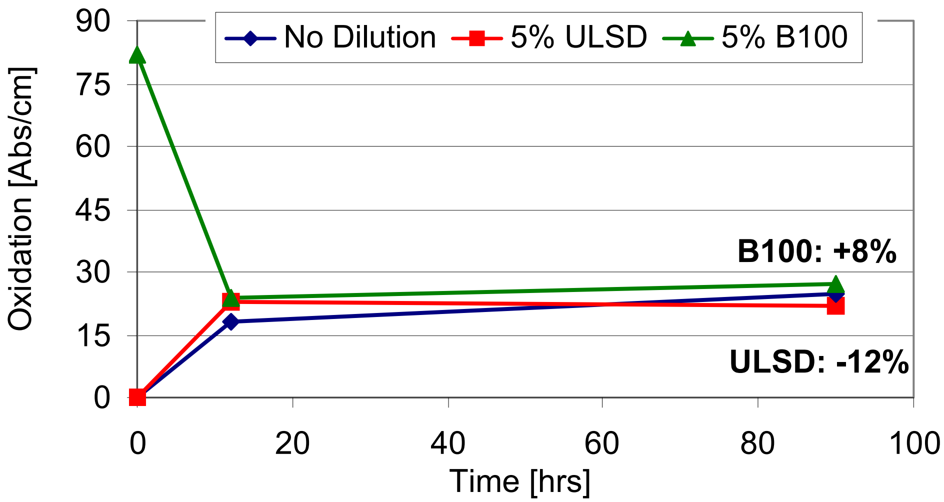
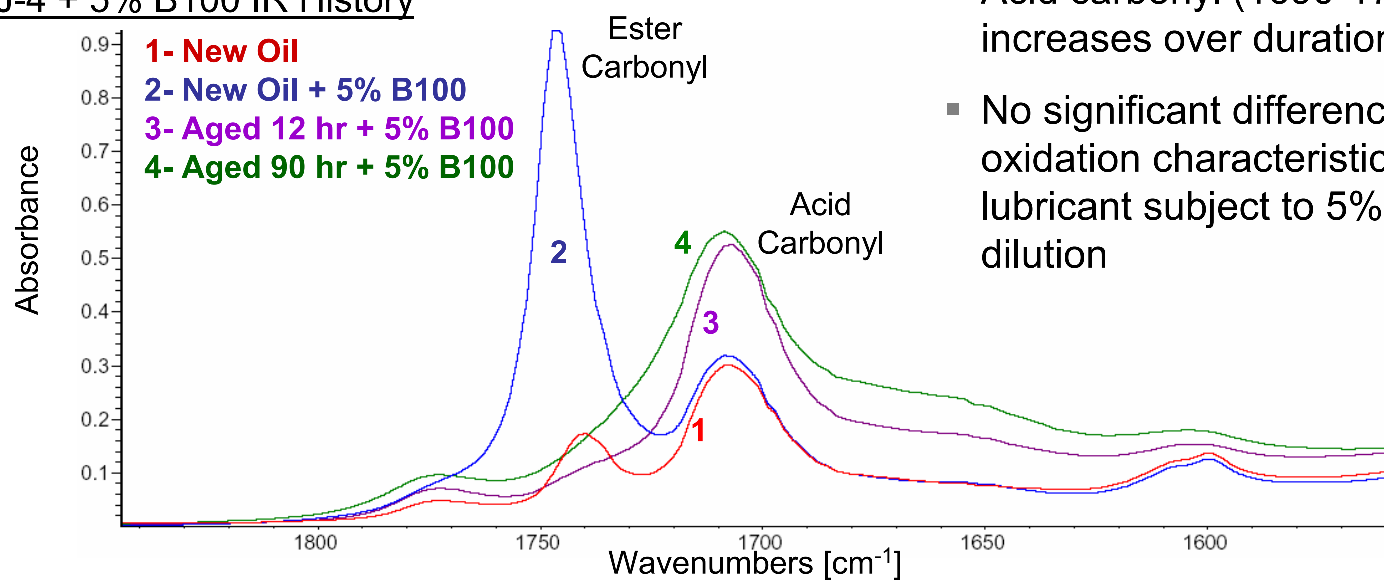
| CJ-4 Oil | Test: 12 hr rapid aged | Condition:165 °C sump, 220 °C inlet |
|---|---|---|
| | Test: 78 hr bench oxidation | Condition: 170 °C, 13 L/h air |




CJ-4 + 5% B100 IR History




- Apparent increase in oxidation in biodiesel fuel dilution case due to ester interference in oxidation (carbonyl) range
- Ester peak disappears following high temperature degradation test indicating B100 loss
- Acid carbonyl (1690-1720 $cm^{-1}$) increases over duration of test
- No significant difference in oxidation characteristics of lubricant subject to 5% B100 fuel dilution

# Biodiesel Interactions with Anti-Wear Additives

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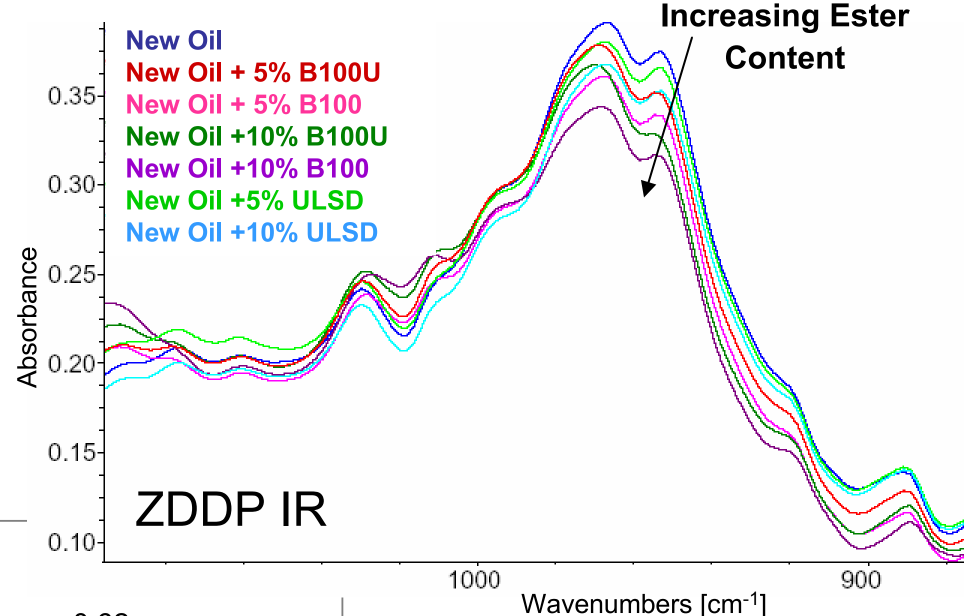
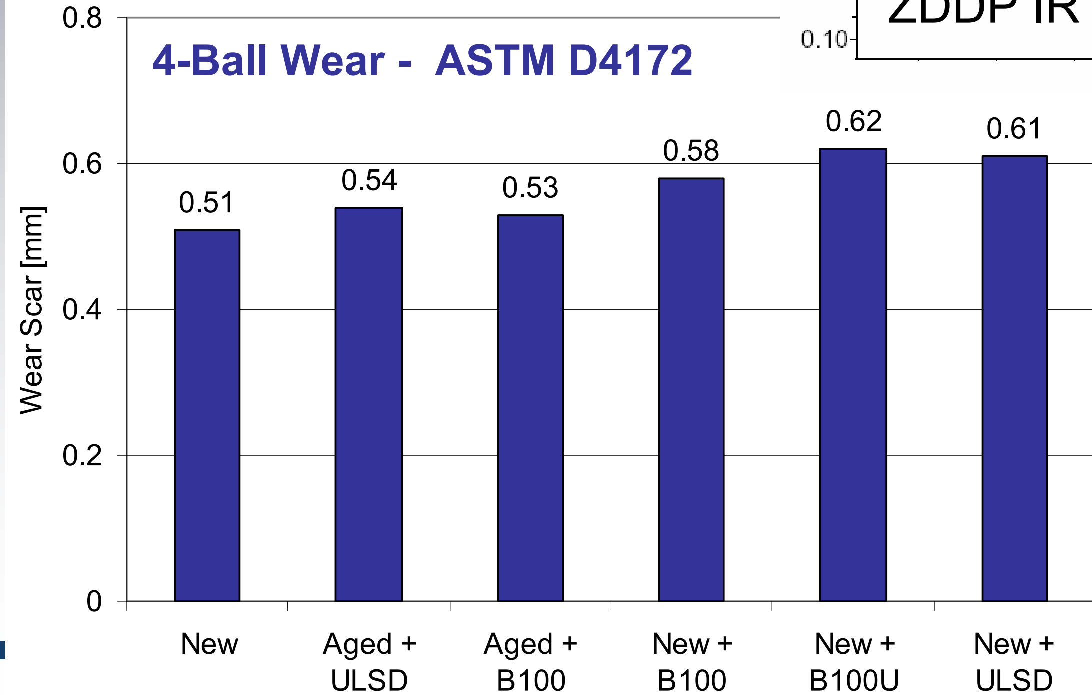
## ZDDP Functionality

- Decreases with increasing ester content in lubricant
- Small dilution effect accounted for with ULSD
- Quantification extremely sensitive to integration range




## Wear Test

- 5% ULSD & B100 in CJ-4
- No significant difference between ULSD and B100 fuel dilution
- Largest effect due to physical dilution of oil independent of fuel

# Conclusions (1)

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## B100 Impact on Emission Aftertreatment Systems

- Reduced PM emissions increase favorable NOx/PM ratio and may reduce DPF regeneration frequency with possible fuel economy benefits
- Potential for trace metals and P in biodiesel below ASTM D6751 mandated level may impact ash loading and catalyst performance
- Increase in ash emissions with B100 SME due to metal debris primarily attributed to solvent properties of fuel
- Elevated levels of metal debris in B100 PM expected to decrease over time with use of B100 in system

# Conclusions (2)

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## B100 Lubricant Fuel Dilution Effects

- Apparent increased oxidation levels of lubricant with B100 fuel dilution attributed to B100 ester peak and not actual lubricant degradation
- Magnitude of biodiesel ester carbonyl interference measurements depends on fuel quality
- Potential for biodiesel ZDDP interaction as evidenced by decrease in ZDDP functionality in FTIR spectra
- Wear tests show no difference in B100 vs. ULSD fuel dilution at 5% fuel dilution levels

**Effects of B100 on lubricant properties and aftertreatment system highly dependent on specific fuel type and composition**

*Short duration use of poor quality fuels can have serious consequences*

# Acknowledgements


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- We thank the following organizations for their support

| | | |
|---|---|---|
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| Ciba Specialty Chemicals | | |

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# Questions…