

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

Comparison with Conventional Diesel Fuel

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Alexander G. Sappok

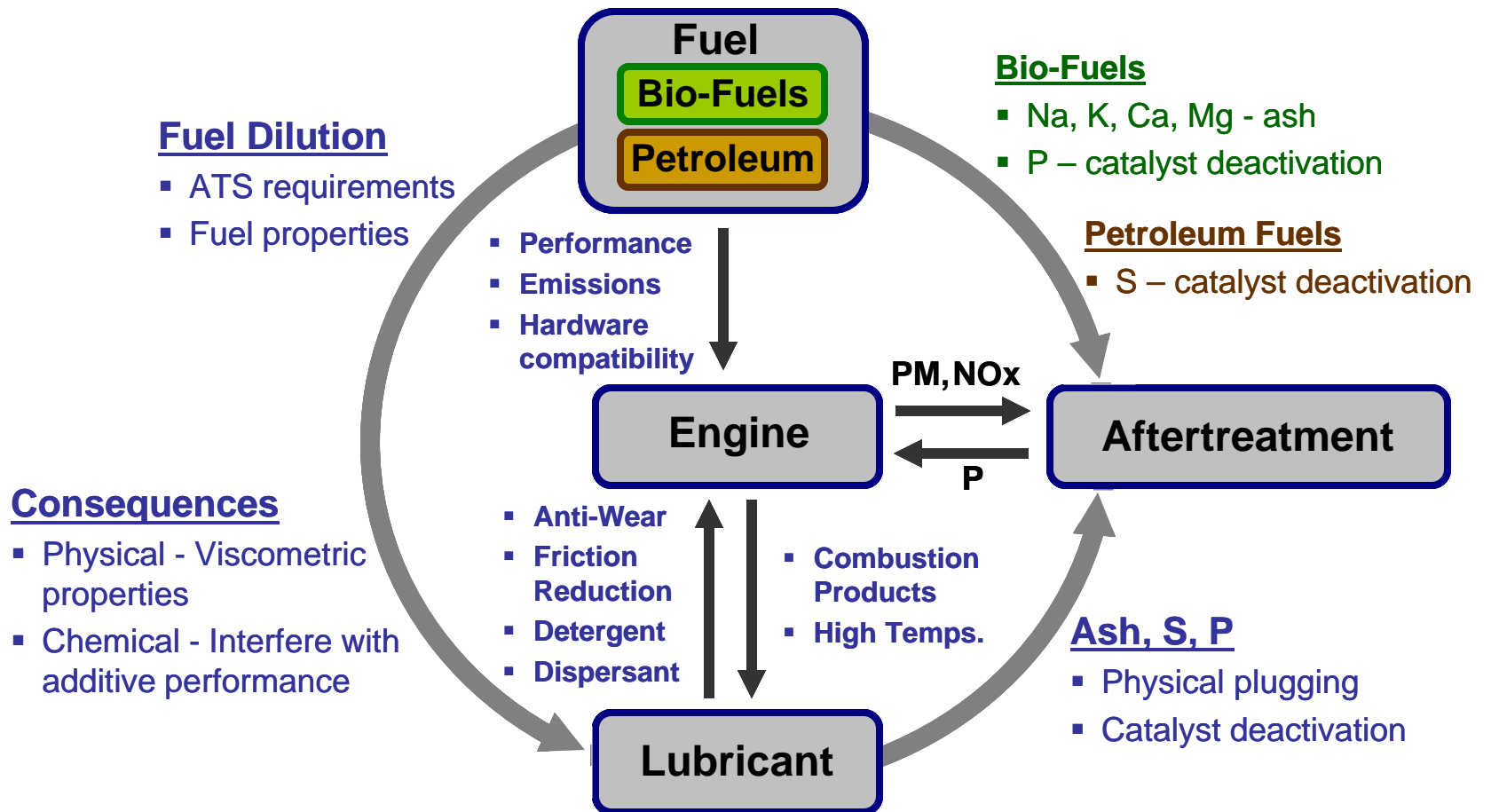
Massachusetts Institute of Technology

Sloan Automotive Laboratory



Motivation

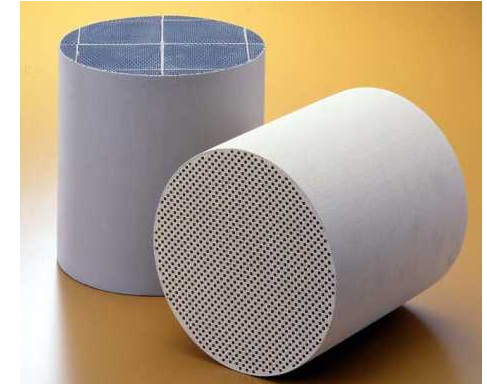
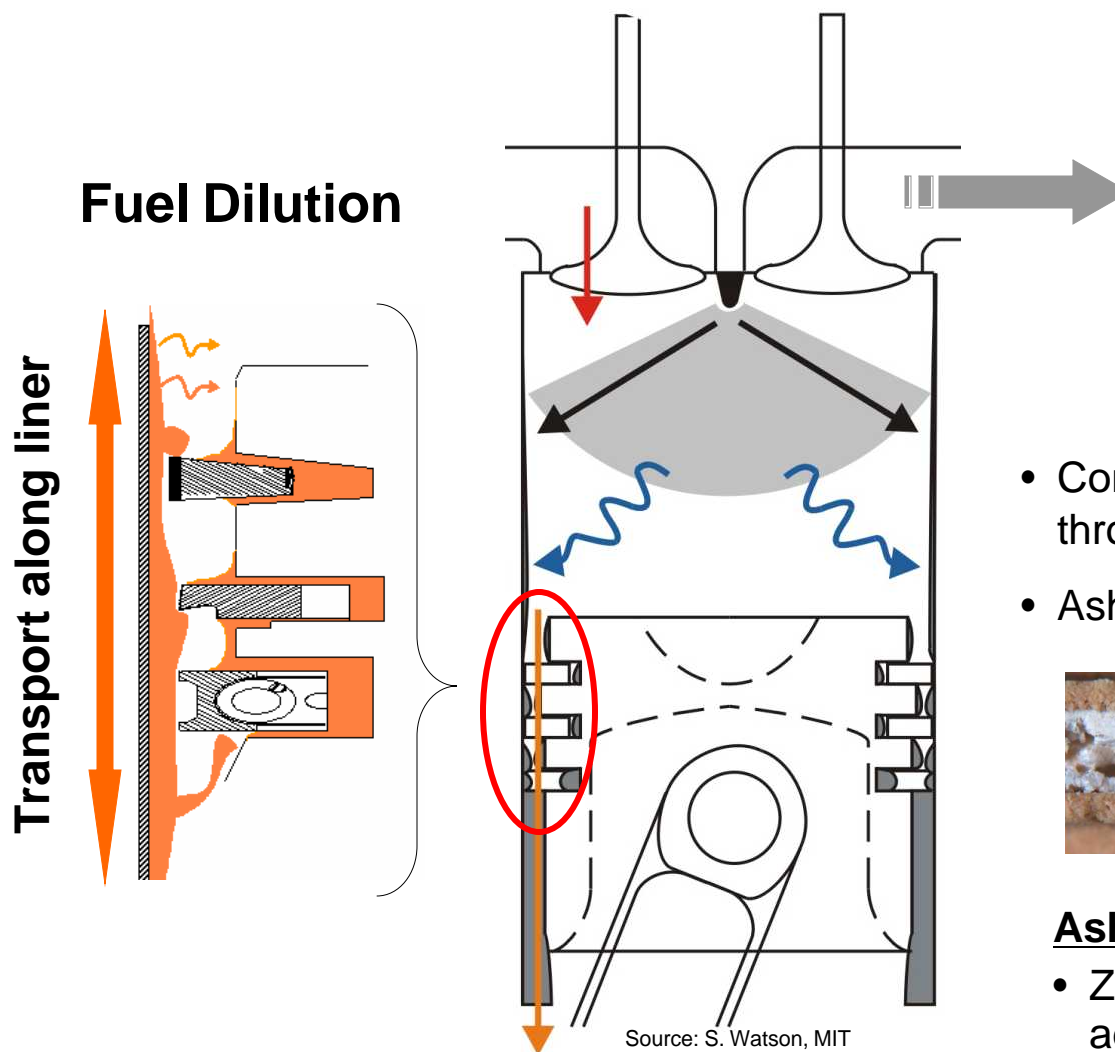
Fuel and lubricant composition affects engine and aftertreatment system (ATS) performance.



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

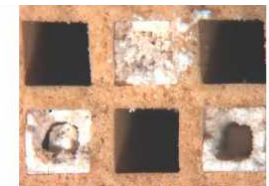
Lubricant Fuel Dilution and Aftertreatment Interactions

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Source: NGK

- Combustion products pass through **aftertreatment system**
- Ash contributes to filter plugging



CORNING

Ash Sources

- Zn, Mg, Ca, S, P in lubricant additives
- Trace metals in fuels
- Engine wear and corrosion

Accumulation of fuel and
combustion products in oil sump



Diesel Engine Lubricant and Fuel Interactions

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■ Diesel Engine Lubricants

- Additive package can be up to 25% of total lubricant*
- Anti-wear (Zn, P, S), detergents (Ca, Mg), and many others
- Minimize ash impact on aftertreatment system

■ Bio-fuel effects on lubricant properties

- Distillation characteristics and boiling range affect amount of fuel that reaches cylinder walls*
- Initial decrease followed by increase in lubricant viscosity due to oxidation and polymerization of fuel constituents (SAE 2005-26-356)
- 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)



* Rudnick, Lubricant Additives Chemistry and Applications

Lubricants and Fuels Affect Aftertreatment Systems

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■ Lubricant Specifications

- CJ-4 oil specification for enhanced compatibility with aftertreatment systems
- Limits lubricant sulfated ash to 1.0% maximum

■ 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 ~ **1,000 ppm_w** in lubricant*
 - Current CJ-4 oils contain ~ 1,000 ppm Zn, P, and Ca each
- Decreased PM emissions
 - Reduce frequency of regeneration
 - Bio-diesel generated PM may oxidize more rapidly

Experimental Apparatus

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❑ Cummins ISB 300

- ❑ Variable geometry turbocharger
- ❑ Cooled EGR
- ❑ Common rail fuel injection
- ❑ Fully electronically controlled

❑ PM Sampling

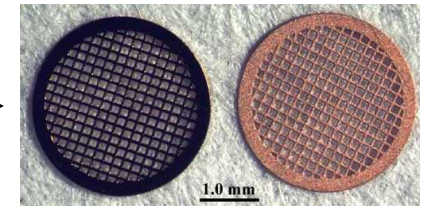
- ❑ Conventional 47 mm filters
- ❑ Individual particulate collection using 3mm dia. TEM grids

❑ Sample Analysis

- ❑ Horiba MEXA 1370 – SOL, SOF, SO₄
- ❑ TGA – Total ash content
- ❑ Scanning Transmission Electron Microscopy (STEM)



2002 Cummins ISB 300

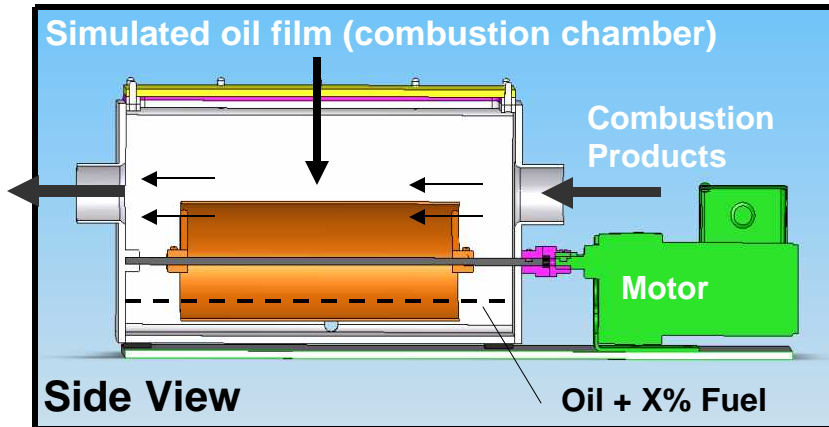


Comparison of conventional 47mm filters and 3mm sample grids

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 test: 48/78 hours

■ Lubricant Analysis

- TAN, TBN, Viscosity, FTIR, ICP
- 4-Ball Wear

Lubricant Composition – 15W-40

Lubricant Elemental Analysis

Lubricant Condition	ASTM D5185							
	B	Ca	Fe	Mg	Mo	P	Zn	S
	[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 Trace Elements

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Element	ASTM D5185				
	Lowest Reporting Value	B100 Batch 1	B100 OS*	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 - OS*	3.36	<130	499	>12
ASTM D6751	0.5 max	130 min	500 max	>3

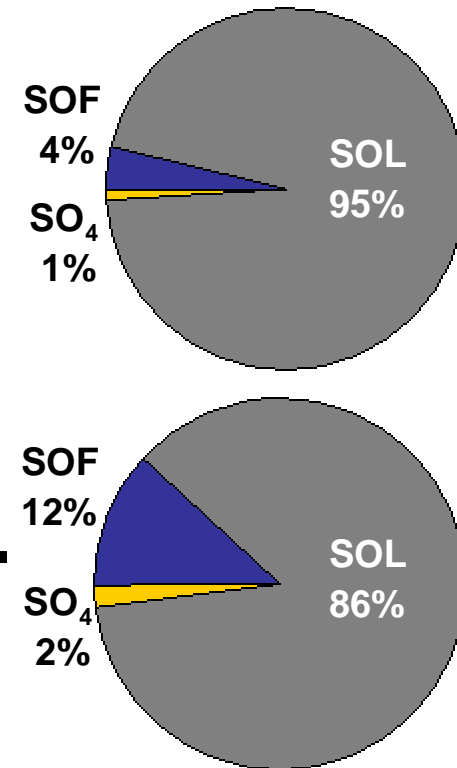
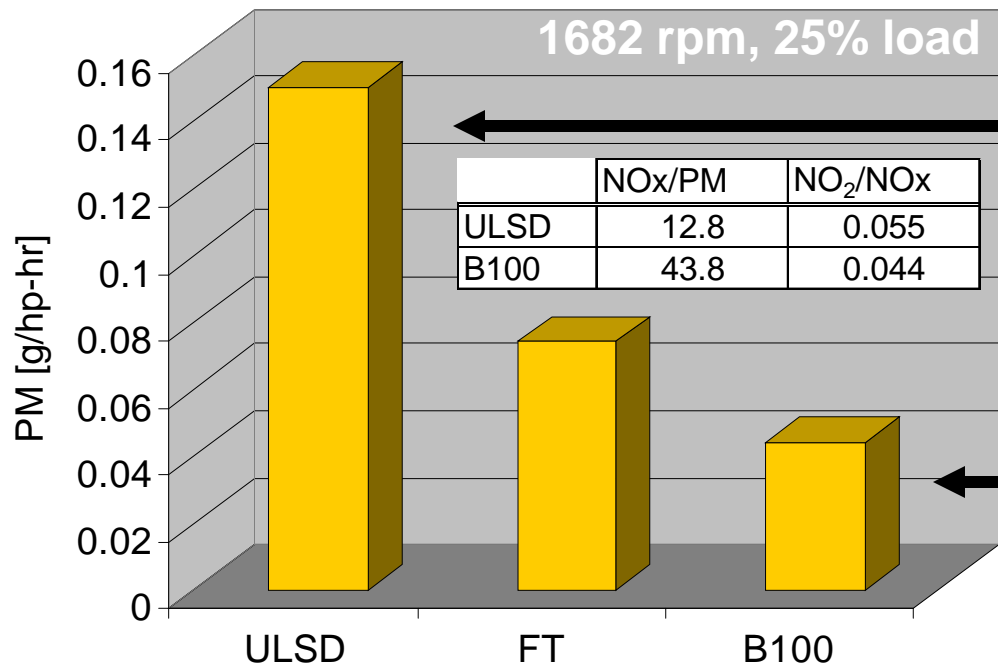
Fuel properties variation for B100 SME

*OS – Out of Specification



B100 Reduces PM Emissions

PM Reduction with B100 SME



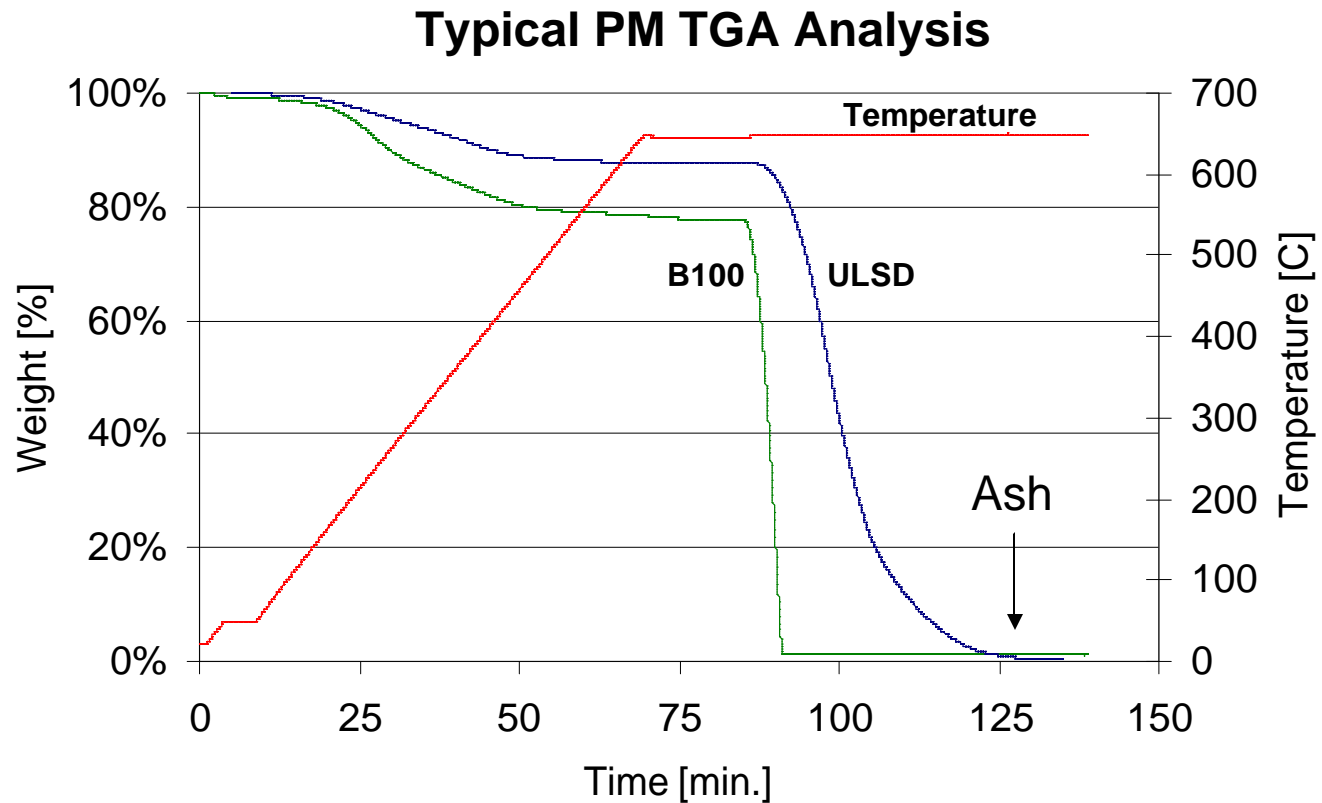
B100 SME shows 70% reduction in PM

- Increase in NOx/PM ratio ~ 3X
- Reduced soot loading of engine 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 with B100

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Ash Fraction

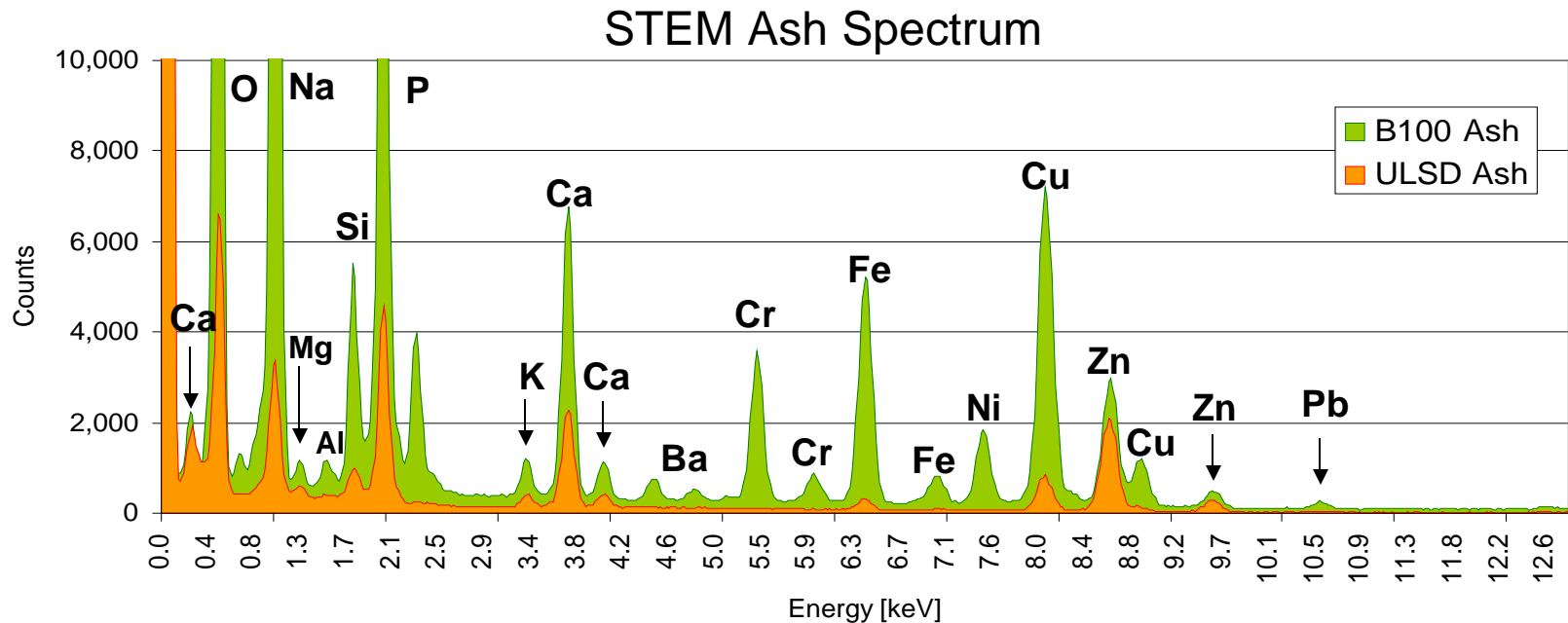
- 1682 rpm, 25% load
- B100 Ash: 1.85% of TPM
- ULSD Ash: 0.44% of TPM

Adjusted Ash Emissions

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

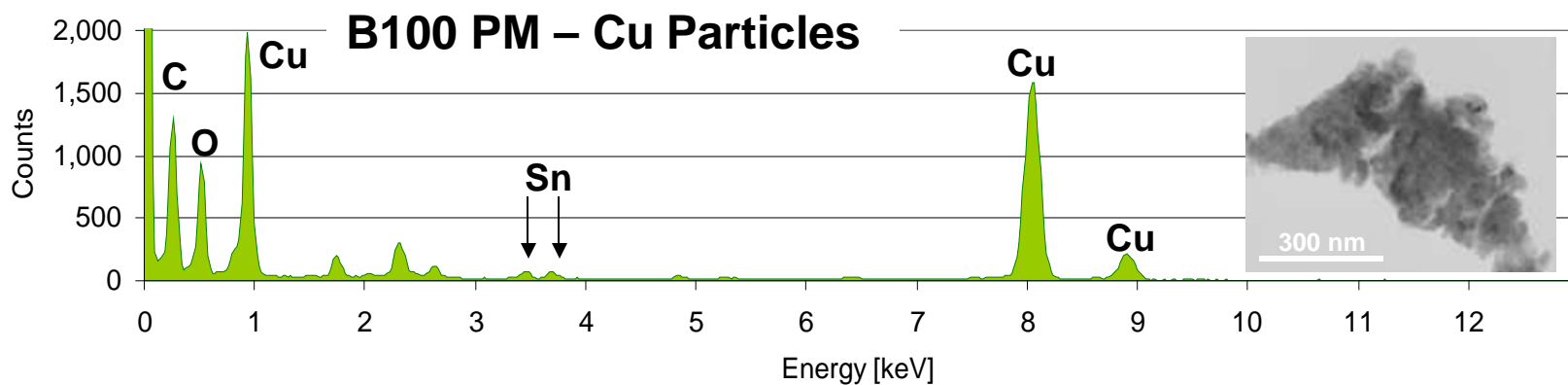
Biodiesel Ash Shows Increased Metals Content

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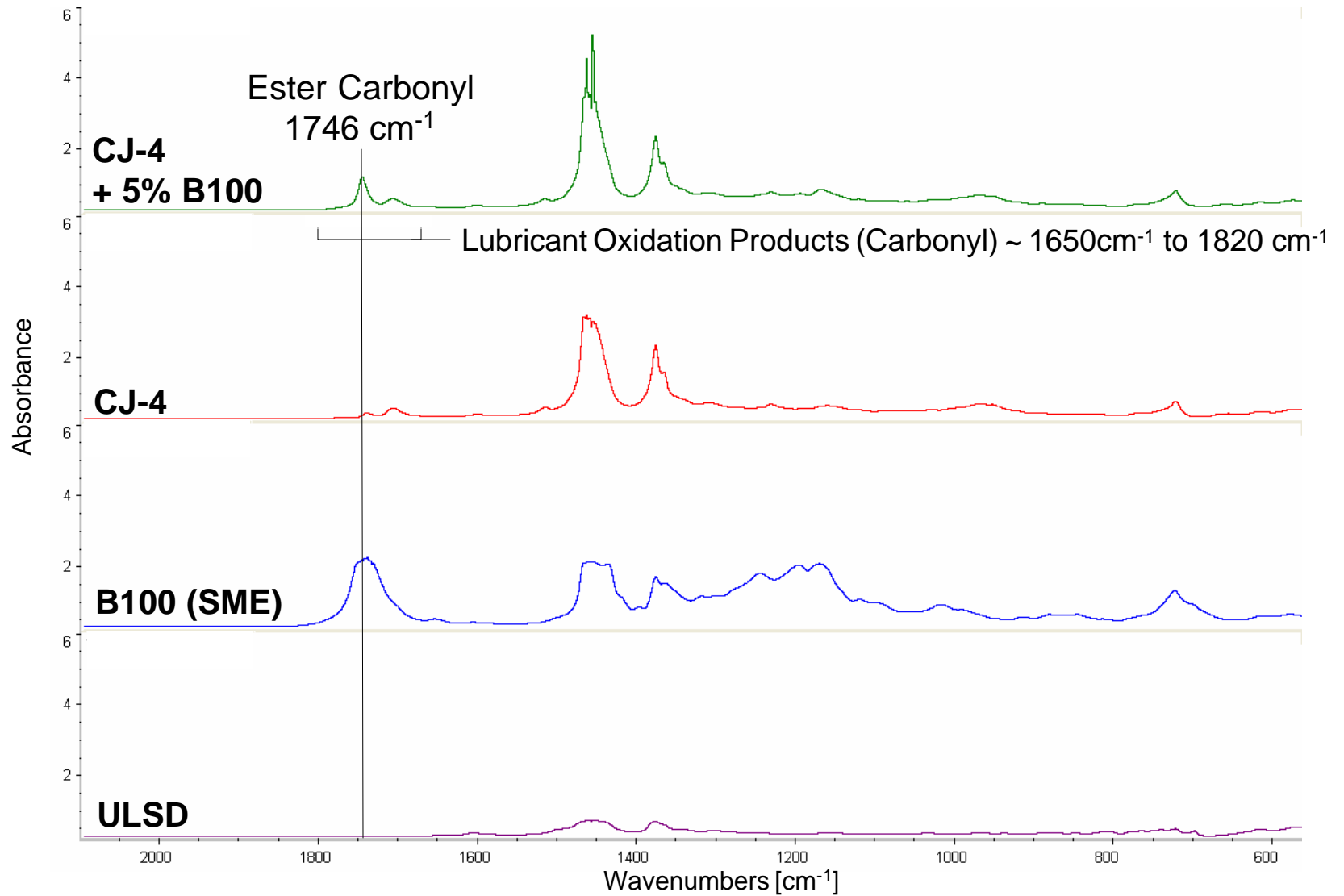
Na and Ca present in biodiesel at higher levels

Debris metals in biodiesel ash possibly due to solvent properties of fuel



FTIR Biodiesel Fuel Dilution

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Biodiesel ester peak can interfere with lubricant oxidation measurements

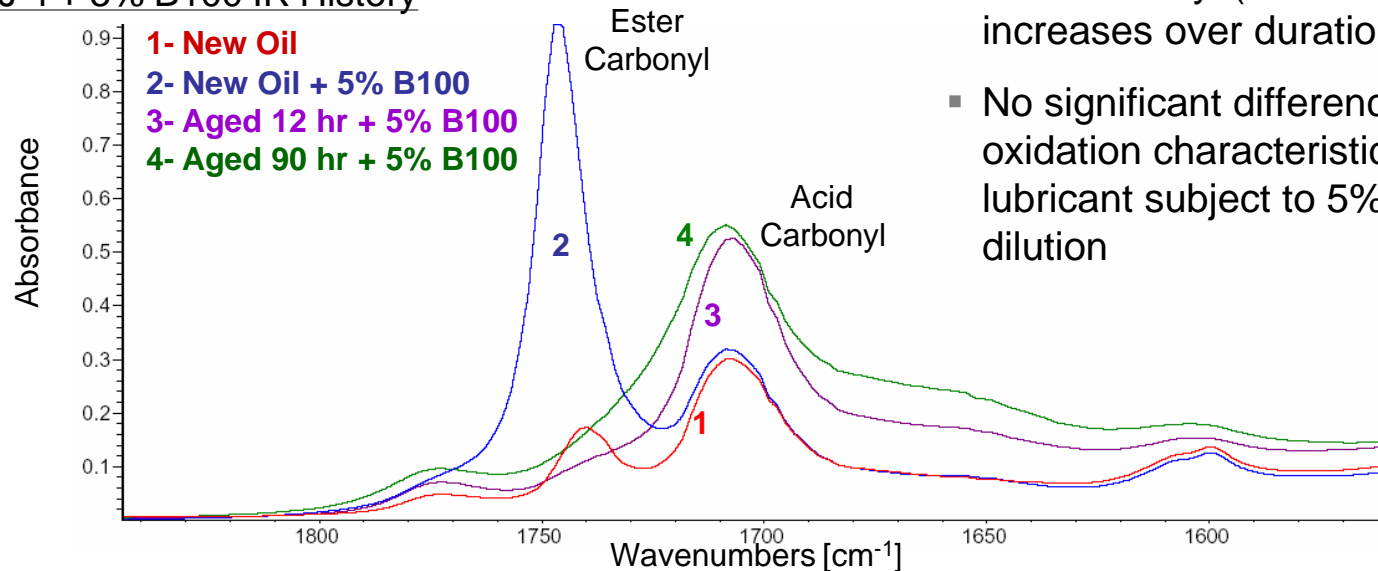
Oxidation Characteristics

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



- 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 ($1690-1720\text{ cm}^{-1}$) increases over duration of test
- No significant difference in oxidation characteristics of lubricant subject to 5% B100 fuel dilution

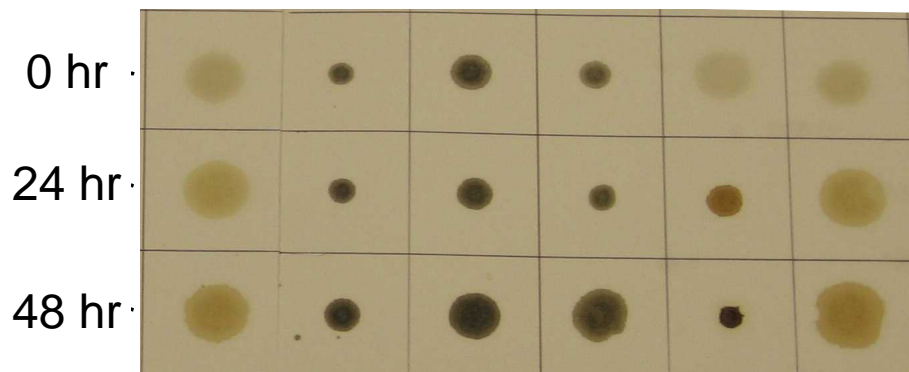
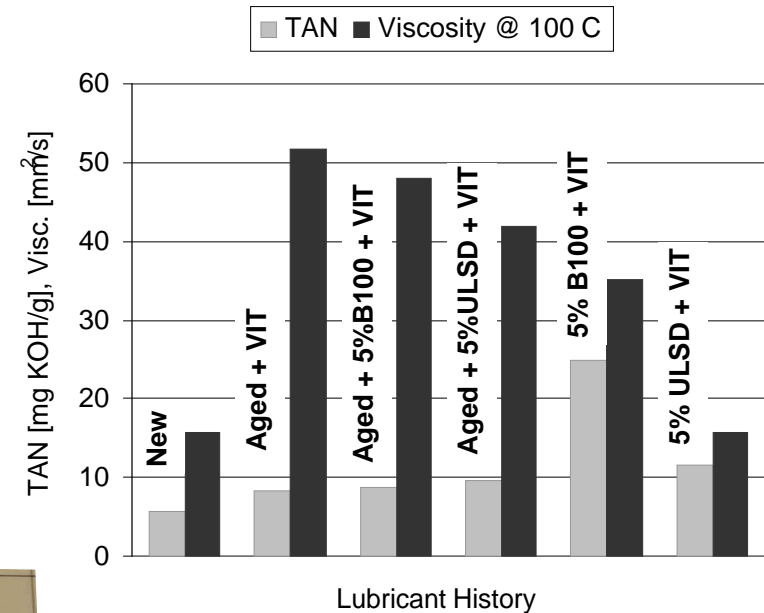
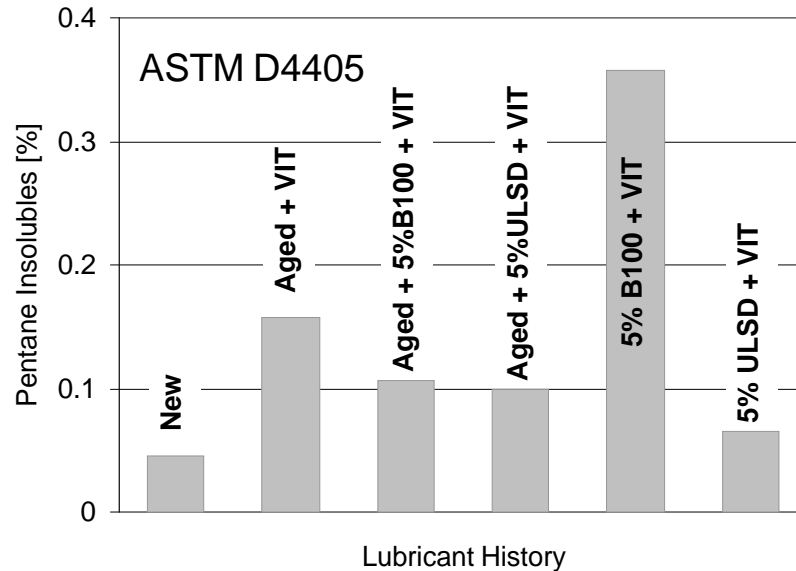
CJ-4 + 5% B100 IR History



Effect on Viscosity and Sludge

CJ-4 Oil Test: 12 hr rapid aged
Test: 48 hr viscosity increase

Condition: 165 °C sump, 220 °C inlet
Condition: 160 °C, 5 L/h O₂, Fe catalyst



- Significant increase in insolubles for new lubricants diluted with B100 and exposed to VIT
- No difference in insolubles for aged lubricants

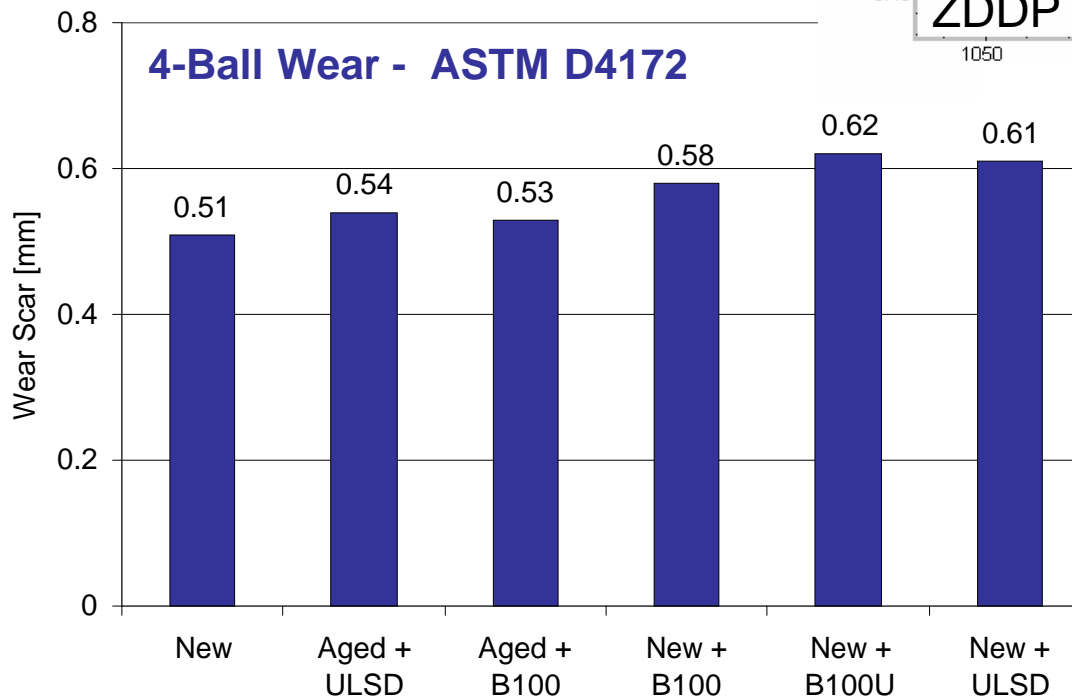
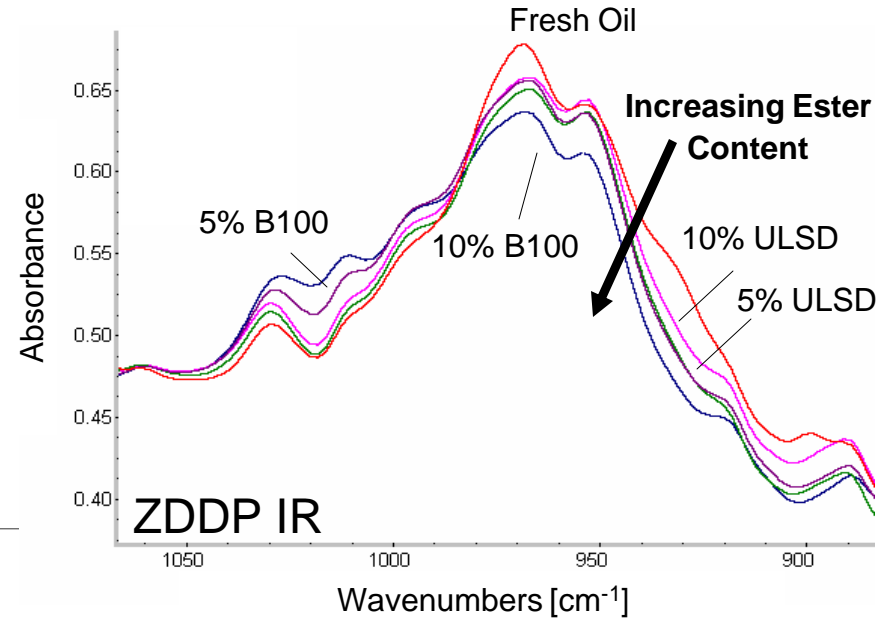
Biodiesel not present in aged oils exposed to high temperatures, but present in new lubricants for VIT test and may increase insolubles.

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)

B100 Impact on Emission Aftertreatment Systems

- Reduced PM emissions increase favorable NO_x/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 Na, and Ca observed in B100 ash and particulates attributed to trace elements in fuel

Conclusions (2)

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
- VIT tests show increased tendency to form sludge with 5% B100
- 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

Acknowledgements

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