

Impact of Biodiesel on the Near-term Performance and Long-term Durability of Advanced Aftertreatment Systems



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Biodiesel's Impact on SCR Performance

NO_x Reduction Ability

Experimental Setup and Objectives

- Compare SCR catalyst performance with ULSD and Soy B20 through engine testing
- Measure relative importance of catalyst temp, exhaust chemistry and catalyst space velocity
- Measure B20's impact on these system variables and overall NO_x conversion
- Focus on Steady-State Modal Testing

Diesel Engine

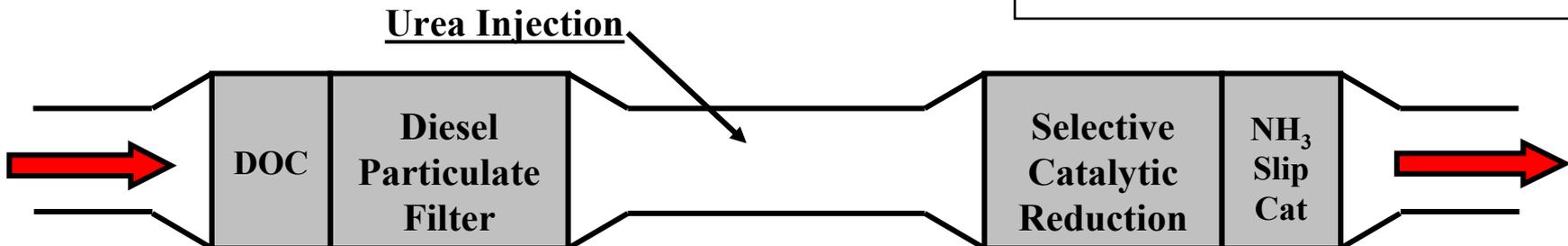
- 2002 Cummins ISB (300 hp)
- 2004 Emissions Cert
- Cooled EGR, VGT, HPCR

Diesel Particulate Filter

- JM CCRT (12 Liters)
- Passively Regenerated
- Pre Catalyst for NO₂ Production

de-NO_x Aftertreatment

- JM Fe-zeolite SCR (15.5 Liters)
- Urea Injection (air assisted)
- NH₃ Slip Catalyst



Critical SCR Performance Variables

8-Mode Test Points

1. SCR Catalyst Temperature
2. NO₂:NO_x Ratio Entering SCR
3. SCR Catalyst Space Velocity

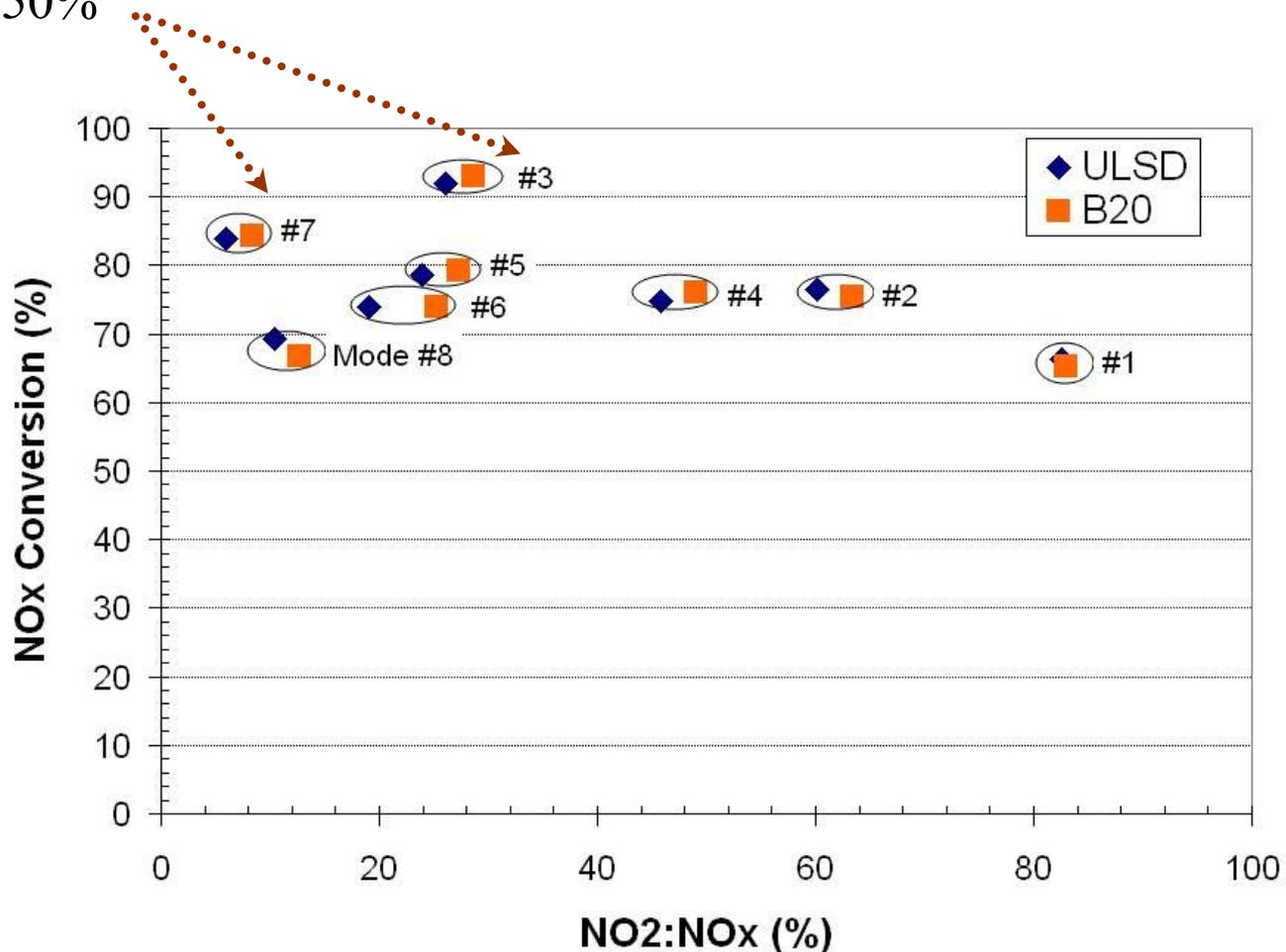
Mode	Speed (rpm)	Torque (ft-lbs)	Temp* (°C)	SV* (1000/hr)	NO ₂ :NO _x * (%)
1	2500	115	299	43	83
2	2412	261	372	48	60
3	1118	306	408	13	26
4	2412	330	415	51	46
5	1700	400	449	34	24
6	1820	450	476	41	19
7	1310	502	523	25	6
8	2308	592	538	57	10

Primary reactions for NO_x reduction by NH₃

- | | |
|--|----------|
| (1) $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ | standard |
| (2) $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$ | fastest |
| (3) $8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$ | slowest |

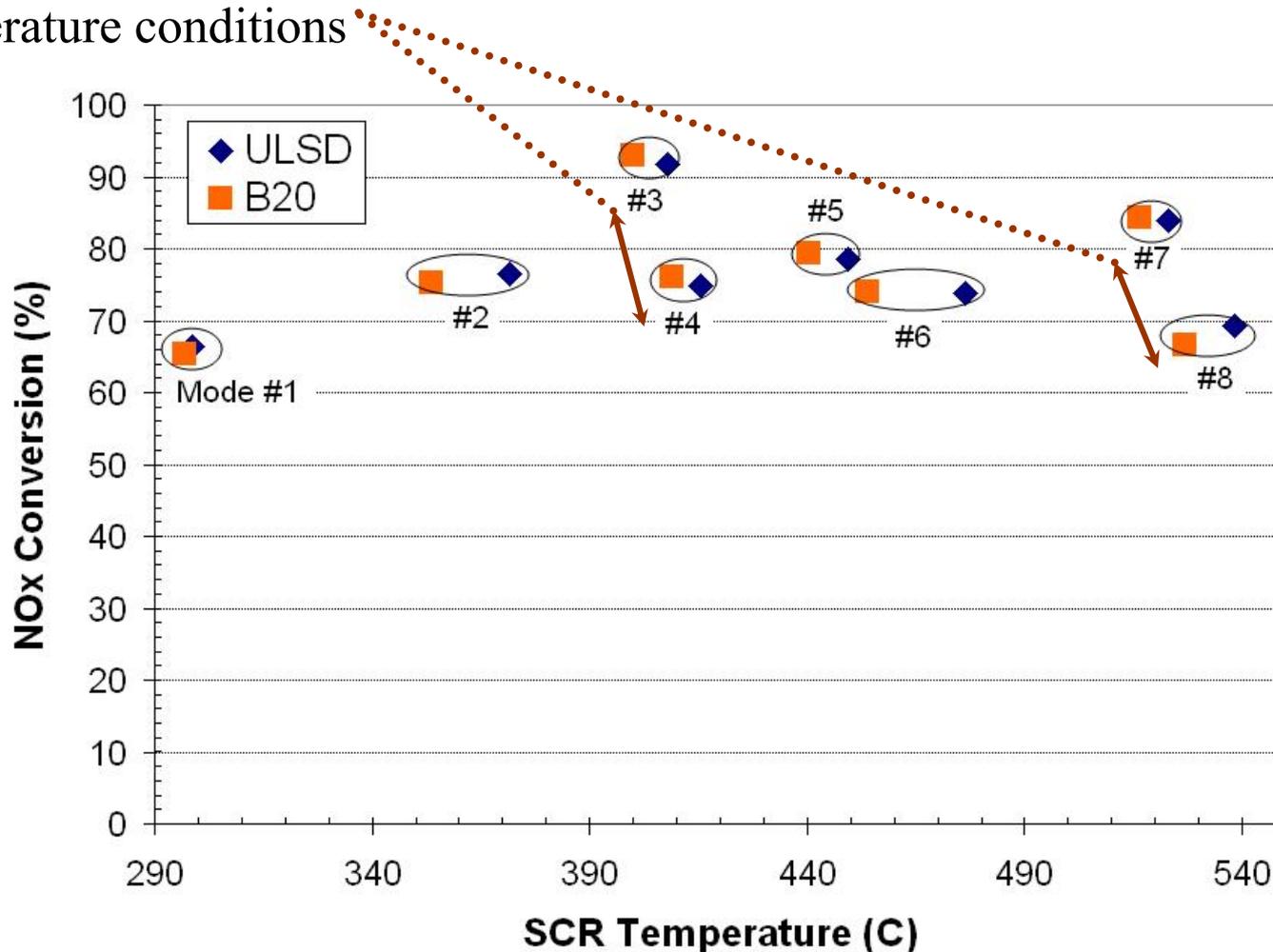
Dependence on $NO_2:NO_x$ Ratio

- B20 created higher $NO_2:NO_x$ ratio (3% on average)
- No distinct trend between NO_x Conversion and $NO_2:NO_x$ ratio
- Modes 3 & 7 showed highest NO_x Conversion even with $NO_2:NO_x$ well below the optimal 50%



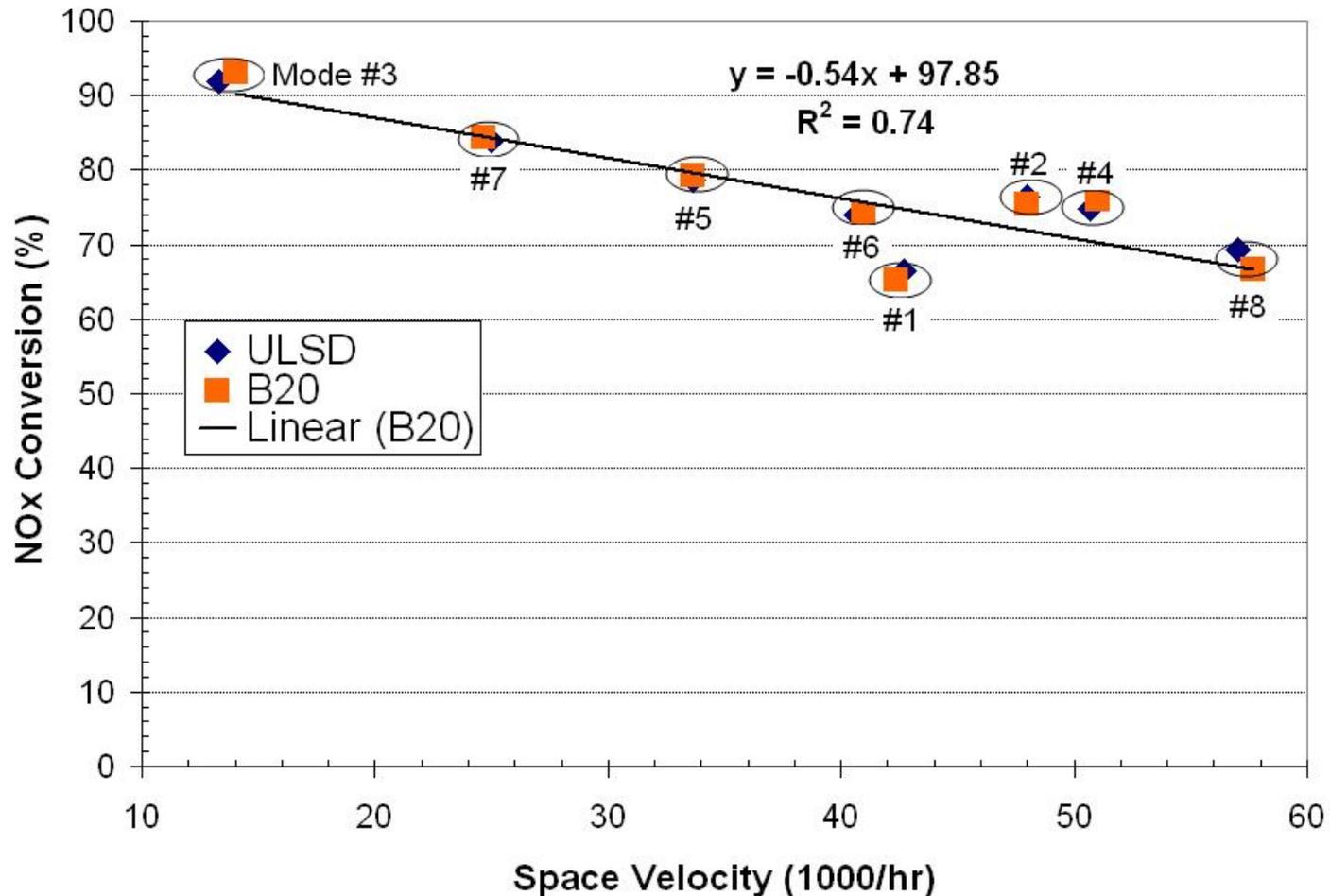
Dependence on SCR Temperature

- ULSD created higher SCR Temperatures (11° C on average)
- No distinct trend between NO_x Conversion and SCR Temperature
- Mode 3 vs 4 & 7 vs 8 – have very different Conversion % under same temperature conditions



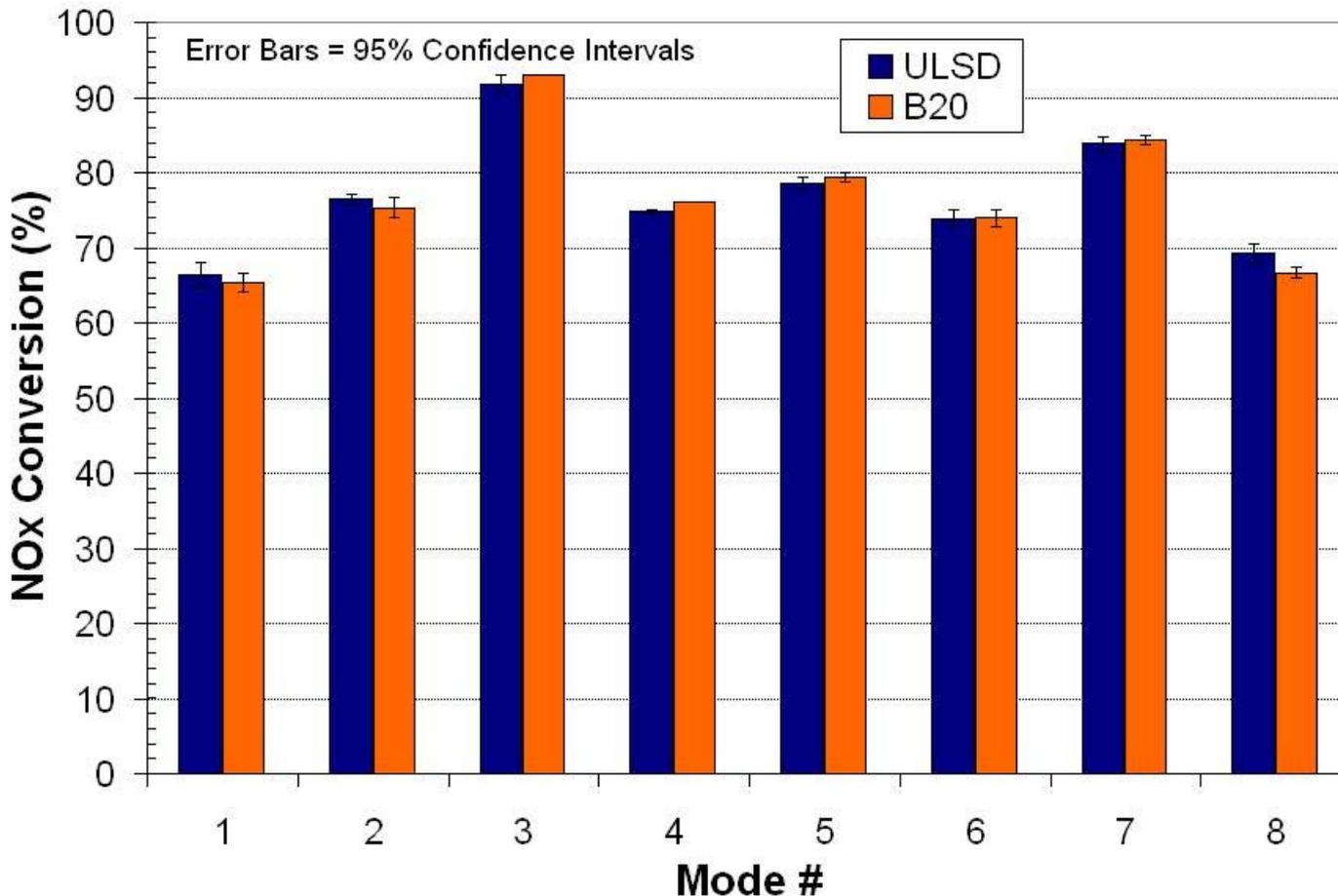
Dependence on Space Velocity

- Space Velocity nearly identical for two fuels
- Distinct linear trend between NO_x Conversion and Space Velocity
- NO_x Conversion drops with decreasing residence time in the catalyst



ULSD vs B20 – Overall NO_x Conversion

- No statistical difference in NO_x Conversion with B20
- Lower Catalyst Temperature and higher NO₂:NO_x have negligible impact on overall NO_x Conversion



Biodiesel Near-term Impacts Literature Review

- “Effect of Biodiesel Blends on Urea Selective Catalytic Reduction Catalyst Performance with a Medium-Duty Engine”. *SAE 2008-01-2484, Aaron Williams et al. – NREL*
- “Effect of Unburned Methyl Esters on the NO_x Conversion of an SCR Catalyst”. *SAE 2009-01-2777, Aaron Williams et al. – NREL*
- “Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particulate Filters”. *Energy & Fuels 2005, Andre L. Boehman et al. – Pennsylvania State University*
- “Effect of Biodiesel Operation on Light-Duty Tier 2 Engine and Emission Control Systems”. *SAE 2008-01-0080, Marek Tatur et al. – FEV Engine Technology*
- “Effect of Biodiesel Blends on Diesel Particulate Filter Performance”. *SAE 2006-01-3280, Aaron Williams et al. – NREL*

Biodiesel's Impact on Exhaust Aftertreatment Durability

The Impact of Alkali Metals

B100 Alkali Ash vs Aftertreatment Full Useful Life

B100 Alkali and Alkaline Metal ASTM limits

Property	ASTM Method	Limits	Units
Ca + Mg	EN 14538	5 max.	ppm
Na + K	EN 14538	5 max.	ppm

**Total Ash Exposure
674 grams**

-Versus-

Aftertreatment Full Useful Life Requirements

Weight Class (lbs. GVW)	OEM Full Useful Life (miles/ yrs)	ARB Retrofit Warranty (miles/ yrs)
Light-duty (<8500)	120,000/10	
Light heavy-duty (8500-19,500)	110,000/10	60,000/5
Medium heavy-duty (19,500-33,000)	185,000/10	100,000/5
Heavy heavy-duty (>33,000)	435,000/10	150,000/5

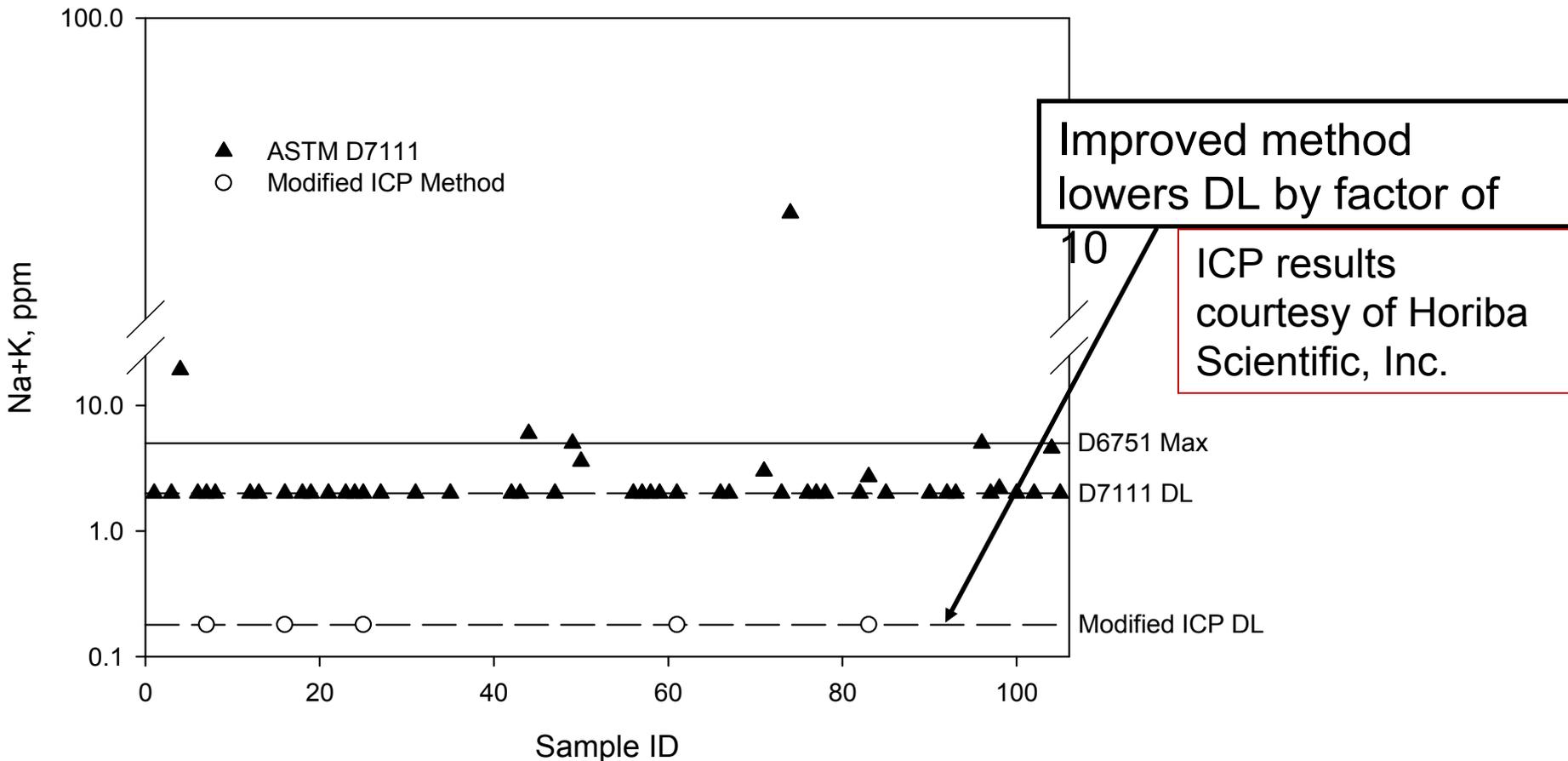
Alkali Impact on Aftertreatment Components

- Alkali and alkaline metals can be detrimental to catalyst durability and performance
 - Alkali attack on SiC protective oxide coating⁽¹⁾
 - Degrade the thermo mechanical properties of catalyst substrates⁽²⁾
 - Deactivation of SCR catalysts⁽³⁾
 - React with alumina washcoat leading to loss of surface area
 - Accumulated ash could eventually plug wall-flow DPF

(1) Choi, Kang, Son, Hwang, SAE 2007-01-1939 (2) Dou and Balland, SAE 2002-01-0734 (3) L. Lisi, G. Lasorella, S. Malloggi and G. Russo, *Applied Catalysis B: Environmental*, 2004, 50, 4, 251-258

NREL Biodiesel Fuel Quality Survey – (Na + K)

- 85% of samples show Na and K below detection limit of standard method (2007 B100 Survey)
- Improved method by lowering detection by factor of 10
- Na+K still below detection for typical samples



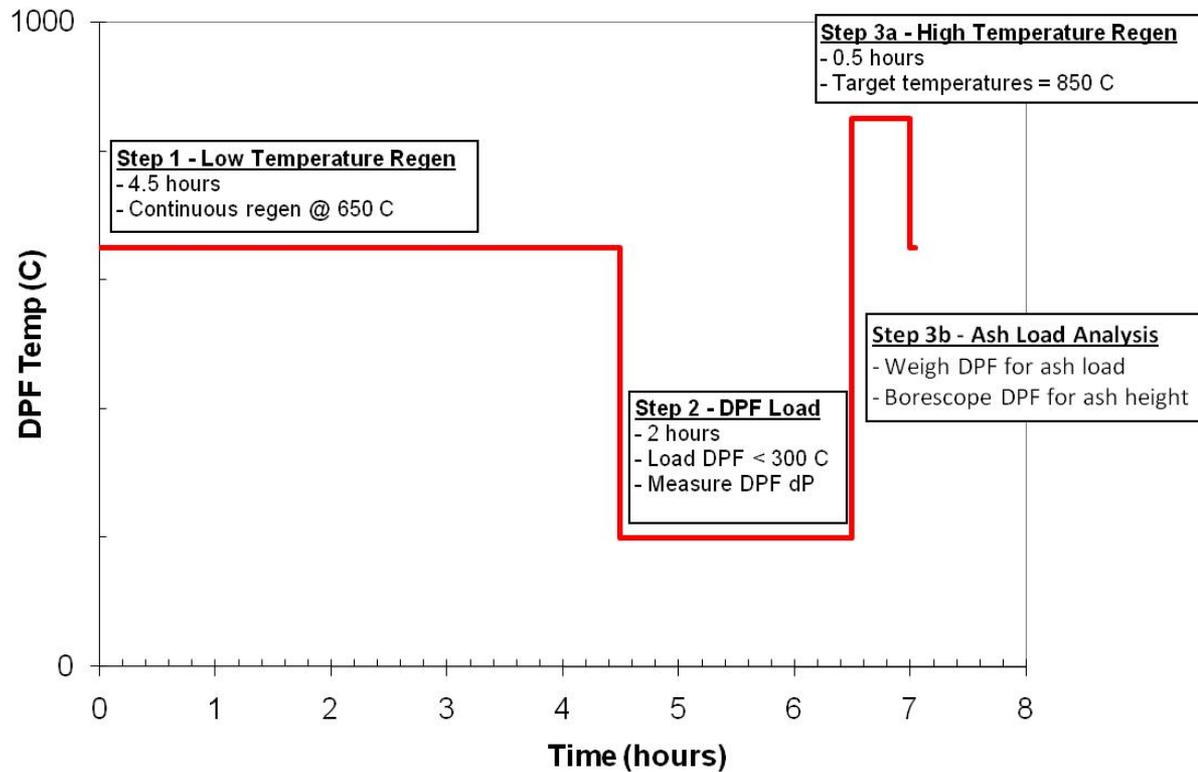
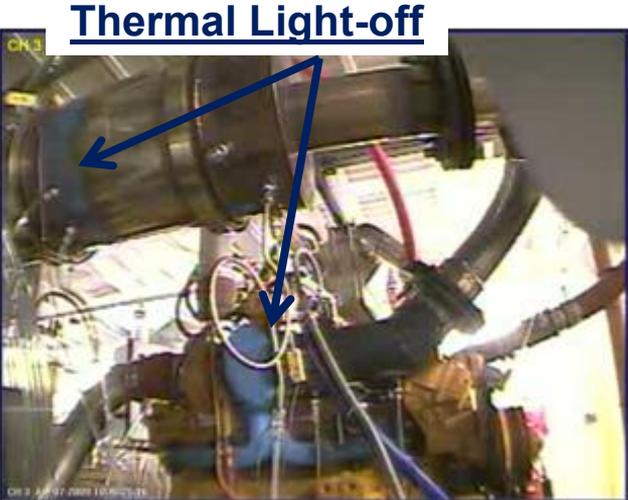
Aftertreatment Durability – Program Goals

- Determine if there is a need for lowering current ASTM standard for metals in biodiesel. *Does current standard effect ash clean interval or durability of a DPF?*
- Ash Accumulation – Match total ash accumulation to 150k mile ash clean interval through accelerated test.
- Thermal Ageing – Match total time of exposure to high regeneration temperatures for 150k miles.



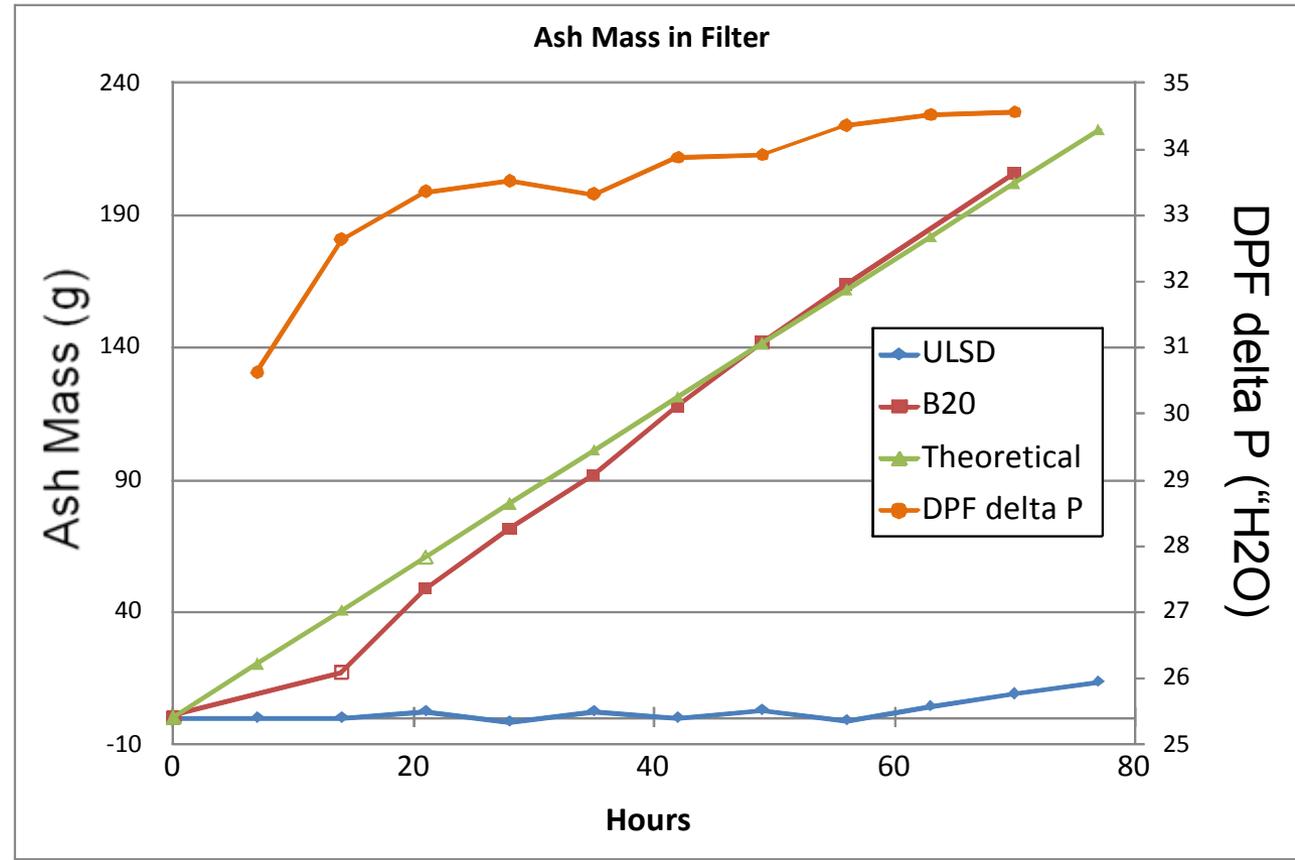
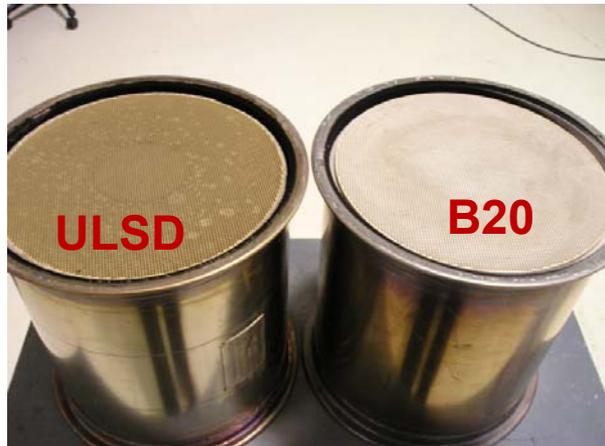
Test Plan

- Achieve 232 grams of biodiesel ash load on DPF
 - Dope fuel with 26x metal spec limit (Ca+Mg = 24ppm, Na+K = 28ppm)
- Achieve 50 hours of regen operation (90% = 650C, 10% = 850C)
 - Use secondary fuel injection for continuous regen conditions at 650C
 - Load DPF then target localized DPF temperatures of 850C
- Repeat 7 hour test cycle – 11 times
- Post mortem analysis



Initial Test Results

- ULSD – Small amount of ash (12 grams) seen from lube oil
- B20 – Ash accumulation closely matches theoretical expectations
- A very fine ash “powder coating” has accumulated on filter face and exhaust pipe walls.
- Only a modest increase in DPF backpressure associated with ash loading.



Summary and Future Research

- B20 causes lower catalyst temperature and higher NO₂:NO_x
- In a space velocity limited system, residence time dominates influence on NO_x conversion
- No change in space velocity with B20 thus no change in NO_x conversion
- Alkali metal limits currently allowed by ASTM spec for biodiesel may be detrimental to aftertreatment durability
- NREL fuel quality survey showed undetectable limits of alkali metals in nearly all biodiesel sampled to date
- Testing underway to determine impact of biodiesel impurities on DPF ash clean interval and durability

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