



Impact of Biodiesel Impurities on the Performance and Durability of DOC, DPF and SCR Technologies

Preprint

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ABSTRACT

It is estimated that operating continuously on a B20 fuel containing the current allowable ASTM specification limits for metal impurities in biodiesel could result in a doubling of ash exposure relative to lube-oil derived ash. The purpose of this study was to determine if a fuel containing metals at the ASTM limits could cause adverse impacts on the performance and durability of diesel emission control systems. An accelerated durability test method was developed to determine the potential impact of these biodiesel impurities. The test program included engine testing with multiple DPF substrate types as well as DOC and SCR catalysts. The results showed no significant degradation in the thermo-mechanical properties of cordierite, aluminum titanate, or silicon carbide DPFs after exposure to 150,000 mile equivalent biodiesel ash and thermal aging. However, exposure of a cordierite DPF to 435,000 mile equivalent aging resulted in a 69% decrease in the thermal shock resistance parameter. It is estimated that the additional ash from 150,000 miles of biodiesel use would also result in a moderate increases in exhaust backpressure for a DPF. A decrease in DOC activity was seen after exposure to 150,000 mile equivalent aging, resulting in higher HC slip and a reduction in NO₂ formation. The metal-zeolite SCR catalyst experienced a slight loss in activity after exposure to 435,000 mile equivalent aging. This catalyst, placed downstream of the DPF, showed a 5% reduction in overall NO_x conversion activity over the HDDT test cycle.

INTRODUCTION

Biodiesel can be made from various renewable sources such as vegetable oil, animal fat, or waste cooking oil. It is produced through transesterification of the oil or fat with methanol, resulting in mono alkyl esters and the co-product glycerin. This process occurs in the presence of a catalyst, typically sodium hydroxide or potassium hydroxide. Following transesterification and separation of the glycerin, the biodiesel must be purified by extraction of the impurities into water or other means. In this process, residual amounts of sodium (Na) or potassium (K) from the catalyst can be left behind. In addition, small amounts of calcium (Ca) or magnesium (Mg) can be added to the fuel from the purification process. These metallic fuel contaminants are converted to oxides, sulfates, hydroxides or carbonates in the combustion process and form an inorganic ash that can be

deposited onto the exhaust emission control devices found in modern diesel engines. Alkali metals are well known poisons for catalysts and have been shown to negatively impact the mechanical properties of ceramic substrates.^[1] Furthermore, alkali metal hydroxides such as sodium and potassium are volatilized in the presence of steam and can therefore penetrate the catalyst washcoat or substrate, or be carried downstream of the diesel particulate filter (DPF) where the solid ash is captured. Of further concern, the increased ash from biodiesel combined with the normal ash from lube-oil could potentially result in excessive levels of ash in the DPF increasing pressure drop and the frequency required for filter maintenance.

Metal impurities are currently limited by ASTM D6751 to 5 parts per million (ppm) of Na+K and 5 ppm of Ca+Mg in B100 (100% biodiesel). While these limits are relatively low, U.S. Environmental Protection Agency (EPA) rules require a minimum ash-clean interval for a DPF of 150,000 miles in heavy-duty applications. Furthermore, the requirement for full-useful-life performance of exhaust emission control systems in heavy-duty diesel engines is up to 435,000 miles. In the simple calculation below, we estimate that a B20 fuel at the current allowable limits for these contaminants could result in approximately 230 grams of additional ash exposure by the 150,000 mile ash-clean interval and approximately 670 grams of additional ash exposure over the 435,000 mile full-useful-life. This would nearly double the ash expected from engine oil lubricant alone. This estimate assumes that the metals are in the form of oxides. However, it is likely that they are in the form of hydroxide-oxide-carbonate-sulfate metal compound mixtures and therefore would have a higher mass than estimated.

Biodiesel ash estimates

Fuel Economy = 6 mpg

0.0003% of B20 becomes oxide ash at current spec limits (10ppm Na+K and Ca+Mg in B100)

*150,000 miles / 6 mpg * 0.0003% * 3.1 kg/gal = 0.232 kg*

*435,000 miles / 6 mpg * 0.0003% * 3.1 kg/gal = 0.674 kg*

Lube-oil ash estimates

Oil consumption rate = 0.03% of fuel consumption

Oil specific gravity = 3.3 kg/gal

Oil ash content (CJ-4) = 1%

*150,000 miles / 6 mpg * 0.03% * 3.3 kg/gal * 1% = 0.248 kg*

*435,000 miles / 6 mpg * 0.03% * 3.3 kg/gal * 1% = 0.718 kg*

The negative impacts of alkali on vanadia selective catalytic reduction (SCR) catalysts used in stationary applications was shown by Lisi and coworkers who exposed the catalyst to 0.18 wt.% of Na resulting in a 40% reduction in nitric oxide (NO) conversion.^[2] A study conducted by Cavataio et al. used a laboratory flow reactor to study the performance of diesel oxidation catalyst (DOC) and SCR catalysts after direct deposition of Na and K from aqueous solution.^[3] This study found a negative impact on the carbon monoxide (CO) and hydrocarbon (HC) light-off temperature for platinum based and zeolite-containing DOCs after Na contamination; as well as significant irreversible deactivation in the oxides of nitrogen (NOx) reduction activity of vanadium and Cu-zeolite containing SCR catalysts. However, a study conducted by Tatur and coworkers aged a light-duty system to a simulated 120,000 miles using a B20 that contained metals at the low levels typical of biodiesel in the marketplace (below 1 ppm for Na and K). They observed no detrimental effects on an SCR, NOx adsorber catalyst, DOC or DPF.^[4,5]

With exposure to high temperatures during a DPF regeneration event, the impurity metals in the ash may diffuse through the washcoat and into the catalyst substrate. This change in ceramic substrate composition can lead to

degradation in the thermal shock resistance of the substrate material, and have long-term durability implications for the DPF. A study conducted by Dou and Balland showed the diffusion of potassium, which was a component of the lean NO_x trap catalyst, into the cordierite substrate.^[1] After the potassium-loaded catalyst was aged on the engine, a measurement of the coefficient of thermal expansion, modulus of rupture, and elastic modulus showed a clear degradation in the thermal shock resistance properties of the material. Cordierite has been shown to react to form a sodium aluminosilicate surface phase at temperatures as low as 700° C, however much higher temperatures were required for destruction of the cordierite by sodium.^[6] Silicon carbide (SiC) substrates have been shown to react with alkali at 800° C if other ash metals are present.^[7]

High levels of ash accumulation in the channels of a DPF could also lead to changes in the backpressure of the device, thus affecting engine performance. Studies conducted by Sappok and Wong investigated the impact of lubricant oil ash on the pressure drop sensitivity of a DPF.^[8,9] These studies show that accumulated ash can form a barrier, which prevents depth filtration of the soot in the pores of the DPF substrate. At ash loadings below 15 g/L, this can have a positive impact by lowering the DPF pressure drop compared to a DPF with no ash loading. However, at loadings higher than 15 g/L, the ash begins to have a negative effect as it occupies a significant portion of the DPF volume. The result is a smaller effective filter volume, which by itself will increase the pressure drop. This change in filter geometry also leads to an increased wall velocity, which can impact the packing density and permeability of the accumulated soot.

Metal Levels from Fuel Quality Survey

A biodiesel fuel quality survey conducted by the National Renewable Energy Laboratory (NREL) in 2007 analyzed 56 B100 samples collected from all major biodiesel producers in the United States for compliance with ASTM D6751.^[10] B100 samples collected from producers around the country represented 70% of biodiesel production that year. Analysis of Na+K levels found that while three samples were above the 5 ppm allowable limit, 85% of the samples were below the detection limit of 1 ppm. Results for Ca+Mg analysis showed that 90% of samples were below the specification limit, with many samples at or below the 0.1 ppm detection limit of the analytical method. While this survey showed most biodiesel was below detection limits for metal impurities, specification limits must still be set to ensure adequate performance of engine and emission control systems. The objective of this study was to determine if adverse impacts can occur at the current specification limits.

EXPERIMENTAL APPROACH

In order to expose the emission control components to 150,000 and 435,000 miles of ash in a reasonable amount of time, an accelerated durability test was developed. Preliminary solubility experiments indicated that B20 containing metals at 27 times the specification limit could be created with appropriate reagents. This elevated level of impurities in the fuel reduced the engine operating time needed to achieve 150,000 and 435,000 mile equivalent ash loadings to an experimentally convenient range. Another important aspect of the aging process was to achieve an appropriate amount of time at regeneration temperatures to adequately simulate potential reactions of ash constituents with the catalyst/filter washcoats and substrates. To accelerate the exposure to high temperatures, the DPF was operated nearly continuously at regeneration temperature conditions. Worst case regeneration temperatures were derived from temperature profiles of uncontrolled regeneration and estimated to be distributed as 90% of the time at 650° C and 10% of the time at 850° C. The high temperature portion of the cycle represents temperature spikes due to uncontrolled regeneration as the soot cake lights-off at the beginning of the regeneration cycle. Temperature spikes can in some cases exceed 1000° C for several seconds which when accumulated over the full-useful-life was assumed to be comparable to a lower temperature for a longer period of time.

Estimates of the appropriate ash loading and time at regeneration temperatures were made based on the following assumptions. These assumptions were based on input from a technical steering committee comprised of emission control manufacturers and engine manufacturers.

Accelerated Ash Loading Assumptions

Engine Fuel Consumption = 37 kg/hr

0.0081% of B20 becomes ash (27× metal in fuel)

77 hrs × 37 kg/hr × 0.0081% = 0.231 kg (ash exposure for EPA-minimum ash-clean interval)

231 hrs × 37 kg/hr × 0.0081% = 0.692 kg (ash exposure for EPA heavy-duty full-useful-life requirement)

Accelerated Thermal Aging Assumptions

Peak temperatures of a DPF regeneration last 10 minutes and occurs every 500 miles

150,000 miles / 500 miles × 10 min = 50 hrs

435,000 miles / 500 miles × 10 min = 145 hrs

Engine and Exhaust Emission Control System

A Caterpillar 2008 C9 ACERT engine was used for testing. This is an 8.8L, 300-hp engine calibrated to meet the Tier III off-road emissions limit. The engine is turbocharged and direct injected, and does not use exhaust emission control in its base configuration. A proprietary 60-hour engine break-in method, supplied by Caterpillar, was used to precondition the engine for emission and durability testing. No emission control devices were used during this engine break-in period. By retrofitting the engine with exhaust emission controls, it served as a platform for exposing various catalysts and filters to biodiesel exhaust gas. The engine was retrofitted with an exhaust fuel injector placed 10 cm downstream of the turbo flange and 122 cm upstream of a diesel oxidation catalyst. In order to make the hot exhaust temperatures typical of a regeneration event, diesel fuel was injected into the exhaust and oxidized over the DOC. The DPF was placed 15 cm downstream of the DOC. The total distance between the turbo flange and the DPF inlet was 147 cm. For one set of aging tests, a metal zeolite SCR catalyst system consisting of two bricks was installed downstream of the DPF. The emission control system was instrumented for measurement of temperatures and pressures at the locations shown in Figure 1. The distance between the DPF and the SCR catalyst was 4.3 meters and was selected to ensure that the SCR would not exceed 650° C during the highest temperature modes. The internal DPF temperatures were measured with 0.032 in. K-type thermocouples inserted into the outlet channels of the DPF. Six internal DPF temperatures were measured as well as DOC-inlet, DPF-inlet and DPF-outlet. In the case of the test that included the SCR catalyst, SCR-inlet and SCR-outlet temperatures were measured. Chevron Delo 400LE SAE 15w-40 engine oil was used for all testing. The engine oil and oil filter were changed at the beginning of each new test.

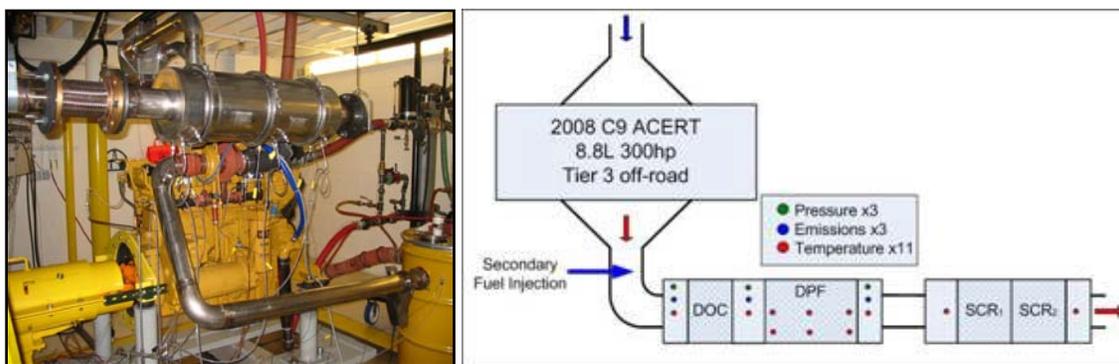


Figure 1. Experimental setup

The engine was operated over a 3-mode steady-state test cycle described in Table 1. The first mode creates an internal DPF temperature of 650° C, representing the normal range of a DPF regeneration event. For this mode, the engine was operated at 2,000 rpm and 1,080 N-m for 4.5 hours. Engine-out exhaust temperatures were around 450° C, and exhaust fuel injection was used to achieve the target temperature of 650° C. The second mode creates DPF temperatures below 300° C, which is low enough to avoid passive regeneration, allowing the filter to collect particulate matter. For this mode, the engine is operated at 2,000 rpm and 272 N-m for 2 hours, allowing for the accumulation of approximately 2.4 g/L of soot. The third mode creates internal DPF temperatures of 850° C, representing the high end of an uncontrolled DPF regeneration event. In this mode, the engine is operated at 1,200 rpm and 1,180 N-m for 0.5 hours. Engine-out exhaust temperatures were around 580° C, while the full 850° C target temperature was achieved through a combination of exhaust fuel injection and combustion of the soot collected on the DPF in mode 2. In order to prevent unintentional uncontrolled regeneration of the stored soot, the temperature ramp rate was controlled to 1° C/sec when transitioning to mode 3. In total, these three modes create a 7-hour test cycle. To achieve the equivalent of 150,000 miles of biodiesel ash accumulation and thermal aging, this 7-hour cycle is repeated 11 times for a total of 77 hours of operation, with 55 hours of operation under DPF regeneration conditions.

The mass of ash collected onto the DPF was monitored throughout the test by weighing the filter every 7 hours. The DPF is weighed after the mode 3 high-temperature regeneration event to ensure that there is no soot on the filter. DPF temperatures were consistently above 200° C at the time of weighing to prevent water adsorption. A second unused DPF was also weighed at the same time to serve as a baseline reference weight.

Table 1. Ash loading test cycle

Engine Mode	Time (hrs)	Speed (rpm)	Load (N-m)	DPF Temp (°C)
1 (low temp regen)	4.5	2,000	1,080	650
2 (soot loading)	2.0	2,000	272	<300
3 (high temp regen)	0.5	1,200	1,180	850

This test cycle was used to expose several different emission control components, listed in Table 2, to biodiesel ash and thermal aging. Three different DPF substrate materials were evaluated, including cordierite, SiC, and aluminum titanate (AT). Each DPF was 17 L in volume and was washcoated to have the same precious metal loading. Each DPF substrate type was tested to 150,000 mile equivalent operation. A pair of cordierite DPFs were also tested to the 435,000 mile equivalent full-useful-life limit. In each case, a baseline test was conducted with ultra low sulfur diesel (ULSD) followed by a test with B20, on a set of equivalent parts, for comparison.

The order of testing along with device type, fuel type and simulated mileage is listed in Table 3. Tests 1 through 3 included a DOC and a DPF. However, in these tests the DOC was used to induce the 850° C DPF temperature, a situation that would not occur in actual use where high DPF temperatures would be generated by rapid combustion of soot. Thus these DOCs were not examined for performance after exposure to the engine exhaust because exposure to this temperature would lead to an inordinate degree of thermal deactivation. A separate catalyst was used for each test. To generate DOCs for post-exposure examination, a set of DOCs were operated only at modes one and two for simulated 150,000 miles of accelerated aging in tests 4a and 4b, avoiding the inordinate degree of thermal deactivation. Thus tests 4a and 4b did not include the 850°C modes for the first simulated 150,000 miles. A new set of DOCs were installed at the 150,000 mile mark (77 hours) and the remainder of these tests included operation at 850°C. The SCR catalysts, located downstream of the DPF, were exposed to the exhaust for the entire duration of tests 4a and 4b. The temperature at the inlet of the SCR catalyst was controlled to below 650°C during the simulated aging.

Table 2. Test parts subjected to accelerated durability test and analysis

Test Piece	D × L (in)	CPSI	Wall (mil)	PGM (g/ft ³)	Pt:Pd
Cordierite DPF	10.5 × 12	200	12	10	2:1
SiC DPF	10.5 × 12	200	16	10	2:1
AT DPF	10.5 × 12	300	13	10	2:1
DOC	10.5 × 6	400	7	40	4:1
SCR	10.5 × 6	300	5	--	--

Table 3. Test order

Test	DPF [†]	Fuel	Simulated Mileage
1a	Cordierite	ULSD	150k
1b	Cordierite	B20	150k
2a	AT	ULSD	150k
2b	AT	B20	150k
3a	SiC	ULSD	150k
3b	SiC	B20	150k
4a*	Cordierite	ULSD	435k
4b*	Cordierite	B20	435k

[†]All tests include DOC. *Test setup also included SCR catalyst.

Test Fuel Preparation

The biodiesel test fuel was a 20% blend of soy-based biodiesel into a commercial ULSD. Impurities were added into the B20 to achieve 27 times the current specification limit of Na+K and Ca+Mg. The commercial liquid detergent Liquinox, manufactured by Alconox, Inc., was used to dope sodium and potassium into the fuel. The sodium in Liquinox is in the form of sodium dodecylbenzenesulfonate. Sulfur and water were unintended additives, with calculated concentrations of 32 ppm and 651 ppm respectively. Calcium was added in the form of calcium naphthenate, which comes dissolved in mineral spirits from Strem Chemicals, Inc. Fuel analysis was conducted prior to testing to confirm the actual amounts of impurities. In addition, fuel samples were collected from the fuel system return line to confirm that the engine fuel filter / water separator did not remove the impurities. Results from a typical fuel analysis are shown in Table 4. As can be seen in the fuel analysis, a small amount of the impurities are captured by the engine fuel filter. To prevent plugging from these added impurities, the engine's fuel filter and water separator were changed before each new test.

Table 4. Additized B20 Fuel Analysis

Metal	Blended Fuel (ppm)	Filtered Fuel (ppm)
Ca	24	21
Mg	<1	<1
Na	21	19
K	7	6
P	<1	<1

RESULTS AND DISCUSSION

A baseline test was conducted with ULSD for each emission control device followed by a test with the high metal content B20. It is important to note that the ULSD aged parts were exposed to the same time/temperature history as the B20 aged parts, and in that sense can serve as valid controls. However, lube-oil ash generation was not accelerated in these tests so the lube-oil ash contribution is the same regardless of fuel type. Lube-oil ash loading represents approximately one oil drain interval for the 150,000 mile simulated parts. Thus, comparisons of the ULSD and B20 test parts at the 150,000 and 435,000 mile test intervals represent the same

amount of thermal aging and lube-oil ash exposure with the only difference being the additional ash that would be seen by using biodiesel.

DPF Ash Loading and Thermal Exposure

The ash accumulation measured throughout the 150,000 mile equivalent durability test for the cordierite filters is illustrated in Figure 2. The final ash loading for all of the DPFs is listed in Table 5. The cordierite DPF tested with ULSD collected 14 grams of ash from lube-oil, while the B20 test piece collected 228 grams of ash. Based on the previously stated assumptions, 150,000 miles of operation with B20 should create 231 grams of ash from the fuel alone. Thus, the biodiesel ash accumulated in this accelerated durability test is close to theoretical expectations. The lube-oil ash accumulation of these experiments, however, does not reflect 150,000 miles as only the fuel based ash accumulation was accelerated. For both fuel types the lube-oil ash contribution corresponds to the actual run time of only 77 hours.

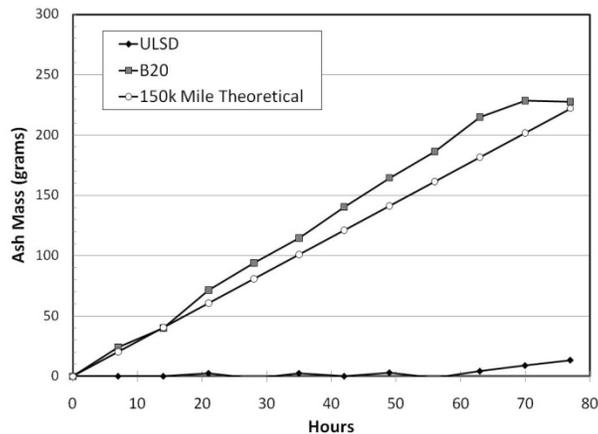


Figure 2. Cordierite DPF ash loading tested to 150,000 mile equivalent

In the case of the cordierite DPF tested to the 435,000 mile equivalent operation, the filter collected ash throughout the entire test period without being cleaned. Under normal operating conditions, much of the ash would be removed from the DPF at the 150,000 mile ash-clean interval. By not cleaning the DPF in this 435,000 mile B20 test, the filter was able to achieve ash loadings closer to those expected from the sum of lube-oil and fuel contributions over 150,000 miles of actual operation. This allows for better evaluation of the impact of high ash loadings on DPF backpressure. Final ash accumulation for the ULSD filter was 124 grams compared to 889 grams for the B20 test piece.

In addition to measuring the mass of ash collected by weighing the DPF, the two cordierite parts aged to the 150,000 mile equivalent operation were also analyzed for ash distribution within the filter. The DPFs were segmented into five axial parts (numbers 1-5) from the inlet to outlet, and further into six radial parts (letters A-F) from the centerline to the edge of the DPF, as shown in Figure 3. These 30 individual segmented parts were analyzed for ash thickness by microscope imaging. The distribution of ash within the DPF is shown in Figure 3. The average ash thickness for the ULSD filter is 0.08 mm compared to 0.15 mm for the B20 filter. In both cases, a small ash plug formed at the outlet of the DPF channels. In the case of the more heavily loaded B20 filter, there is a uniform distribution of ash from segment #1 (inlet) to segment #4, with a consistent thickness of 0.1 mm. This uniform distribution of ash, referred to as wall-ash, is more common in applications that utilize continuous DPF regeneration conditions.^[8] On the other hand, applications that experience periodic regeneration events tend to collect ash at the outlet of the DPF, forming plug-ash. Under real world operating conditions, the ash is incorporated into the soot as particulate matter agglomerates. In the case of a periodically regenerated system, these particulate matter agglomerates build up along the DPF channel walls. A regeneration

event then burns the soot portion of the agglomerate, releasing the ash, which is carried to the end of the DPF channel, forming the ash plug. While small ash plugs have formed, the nearly uniform distribution of ash for the B20 filter indicates that these accelerated durability tests are more representative of a continuously regenerated system.

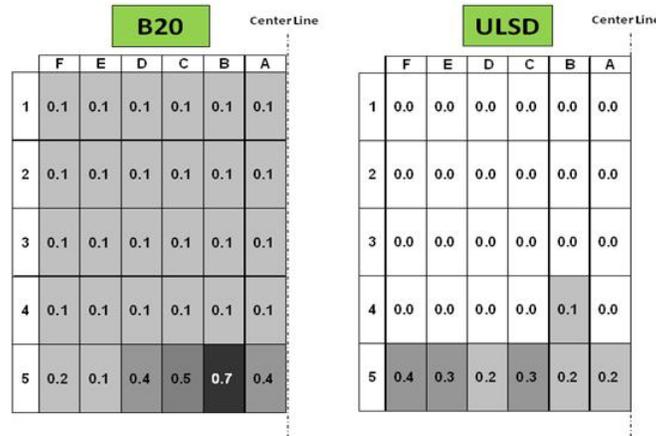


Figure 3. Cordierite DPF ash distribution (ash thickness in mm)

Plots of an internal DPF temperature for the SiC ULSD and B20 DPFs are shown in Figure 4. A temperature history and average overall temperatures for all of the tests are presented in Table 5. Average temperatures and temperature history data show that temperatures were fairly consistent for each DPF pair. Average DPF temperatures were only slightly higher for B20: 11°C for cordierite, 7°C for SiC, and 1°C for AT. The total time spent above 650°C was fairly consistent for all DPFs, ranging from 52.7 hours to 54.2 hours.

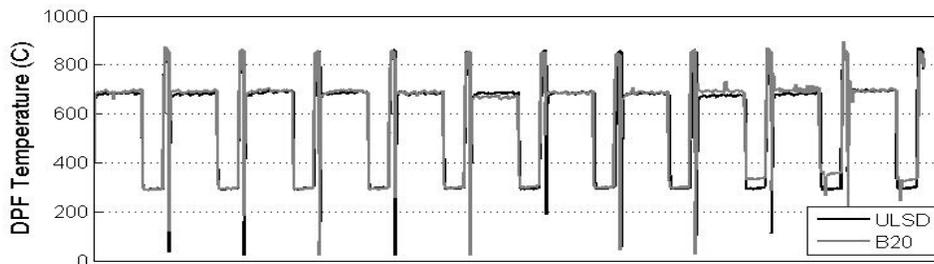


Figure 4. 150,000 mile accelerated durability test – DPF temperature profiles

Table 5. DPF Ash Loading and Thermal Exposure

	Units	Cord.		SiC		AT		Cord. ^a	
		ULSD	B20	ULSD	B20	ULSD	B20	ULSD	B20
Ash loading	g/L	0.8	13.4	2.3	17.1	2.2	12.2	7.3	52.3
DPF T (avg)	°C	565	576	576	583	598	599	599	602
<650°C	hours	25.0	26.6	24.4	24.7	24.2	24.4	72.9	74.4
650°C to 750°C	hours	48.8	49.5	49.3	49.5	49.6	49.6	152.7	153.2
750°C to 875°C	hours	4.4	4.6	4.6	4.4	4.9	4.6	9.5	9.2

^a Accelerated durability tests conducted to 435,000 miles

Impact of Biodiesel Ash on DPF Backpressure

After completing the accelerated aging, a set of engine experiments were used to determine the impact of ash loading on DPF pressure drop. Pressure drop experiments were conducted with the two cordierite DPFs tested to the 435,000 mile equivalent operation. Each of the ash loaded DPFs were further loaded with soot while the pressure drop was monitored across the filter. Pressure drop was measured at three different engine conditions which created DPF space velocities of 23,882 hr^{-1} , 34,588 hr^{-1} and 38,294 hr^{-1} (space velocity based on measured exhaust flow at standard temperature and pressure). The DPF was weighed during this experiment to determine the amount of soot loading. Pressure drop data for both filters is shown in Figure 5 as a function of soot loading.

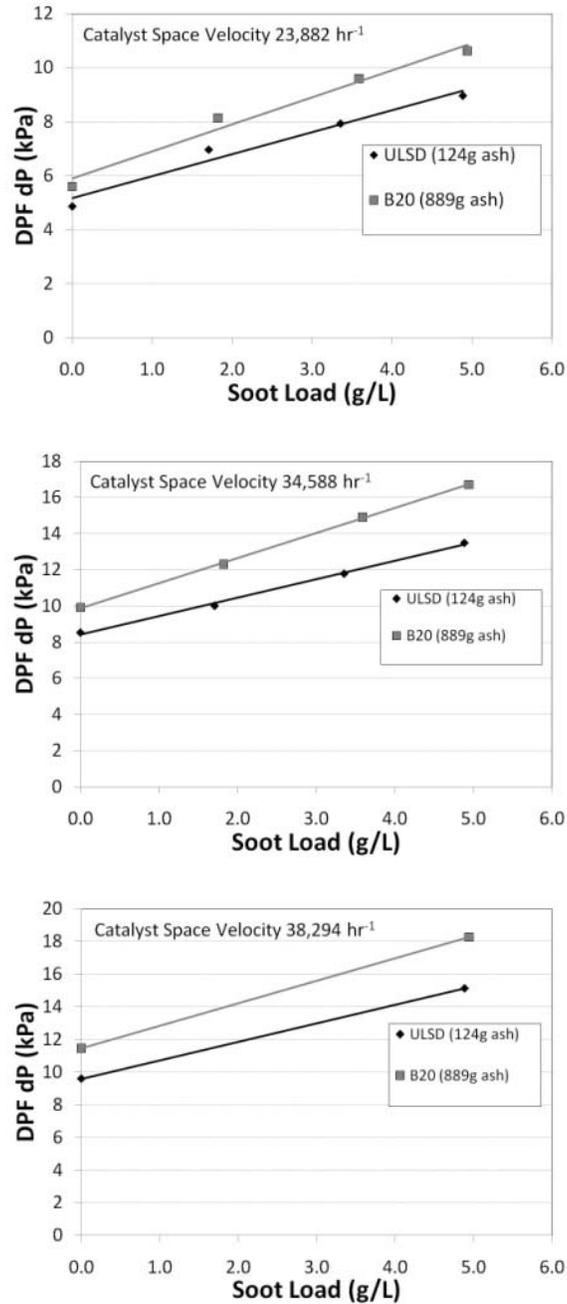


Figure 5. Cordierite DPF pressure drop as a function of soot load, measured at three space velocities

Both of the filters demonstrated a single, distinct linear increase in pressure drop as the soot load was increased from 0 g/L to 5 g/L. Typically, a DPF free of ash loading would show two pressure drop regimes: (1) an initial steep rise in pressure drop as the DPF undergoes depth filtration of the soot, (2) followed by a more modest rise in pressure drop as a cake layer of soot is formed.^[11] These two regimes of soot filtration are illustrated in Figure 6. In the case of these test filters, the layer of ash is most likely preventing depth filtration, which results in the single, more moderate regime of cake filtration. Also of note is that the more heavily ash loaded filter has a steeper increase in backpressure, indicating more sensitivity to soot loading. This is consistent with findings by Sappok and Wong, who show that higher ash loadings have a geometric effect on the DPF, lowering the effective filter volume.^[9] This leads to increased wall velocities, which changes the permeability and packing density of the soot, and hence increased pressure drop.

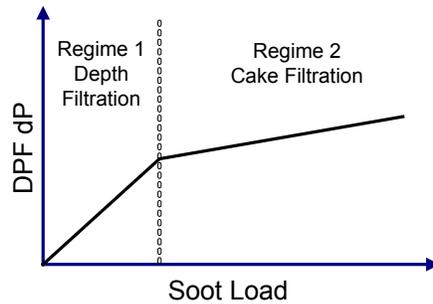


Figure 6. Illustration of soot loading regimes

In the 435,000 mile equivalent operation, the ULSD test filter collected 7.3 g/L of lube-oil ash. To demonstrate the impact of higher ash loading, the B20 filter was operated to the full-useful-life limit of 435,000 miles without ash removal. The ash loading of this filter reached 52.3 g/L. It is important to note that this study did not accelerate the ash accumulation from lube-oil. Thus, these loadings represent the additional ash loading expected with the use of B20. Pressure drop data from these low-ash-load and high-ash-load filters were used to estimate pressure drop at the EPA minimum 150,000 mile ash clean interval. Figure 7 shows the pressure drop across these two test filters with an additional 5 g/L soot loading, at the highest space velocity condition. Using the assumptions presented in the Introduction of this paper, it is estimated that 150,000 miles of operation with B20 would result in 28.2 g/L of ash with contributions from both lube-oil and fuel, while ULSD would result in 15.0 g/L of lube-oil ash. Assuming a linear trend of increasing pressure drop between the filters tested in this study, we estimate that 150,000 miles of operation with B20 would result in a 6.8% increase in backpressure, compared to equivalent operation with ULSD.

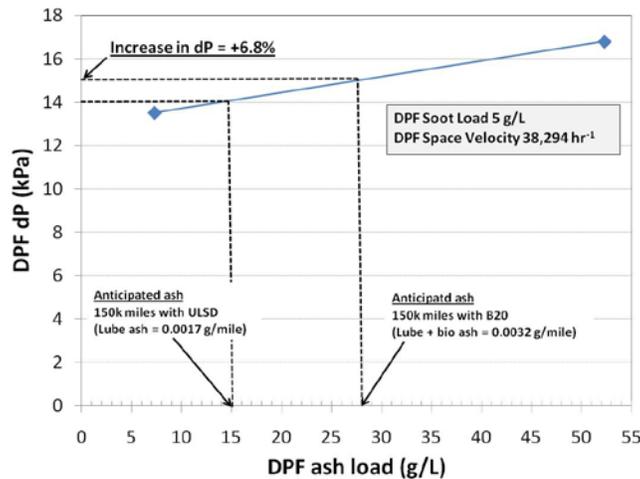


Figure 7. DPF pressure drop as a function of ash load

Impact of Biodiesel Ash on DPF Thermal Shock Resistance Parameter

Previous studies have shown that exposure to alkali and alkaline earth metals can impact the long-term mechanical durability of catalyst substrates.^[1,7] The thermal shock resistance parameter (R_s) of a DPF is a measure of the substrate's ability to withstand rapid changes in temperature such as those experienced during active regeneration events. Resistance to thermal shock for a given material can be calculated by Equation 1. A decrease in the bend strength of the material or an increase in the elastic modulus or the coefficient of thermal expansion will result in a lower thermal shock resistance parameter.

$$R_s = \frac{\lambda \times \sigma}{\alpha \times E} \quad (1)$$

where:

R_s = thermal shock resistance

λ = thermal conductivity

σ = bend strength or modulus of rupture (MOR)

α = coefficient of thermal expansion (CTE)

E = elastic modulus

The cordierite DPFs tested to the 150,000 mile equivalent and 435,000 mile equivalent aging were characterized by the manufacturer. Test parts were cut from the DPF at the inlet, middle and outlet for thermo-mechanical characterization. Three measurements were made at each location and the minimum and maximum values were used to establish the error bars shown in Figure 8. A four-point single notched beam test was used to measure the modulus of rupture, also known as bend strength. The elastic modulus was measured using an acoustic resonance method, and the coefficient of thermal expansion was measured by a dilatometer from 40° to 800° C. Results are shown in Table 6 and Figure 8.

Table 6. Thermo-mechanical properties of B20 cordierite DPF (percent change versus ULSD DPF)

	150k mile			435k mile		
	MOR	E	CTE	MOR	E	CTE
inlet	-5.9	2.3	11.9	42.6	64.3	162.0
middle	-9.3	0.0	-9.5	38.0	63.4	98.6
outlet	2.1	23.3	40.5	65.6	88.7	204.2

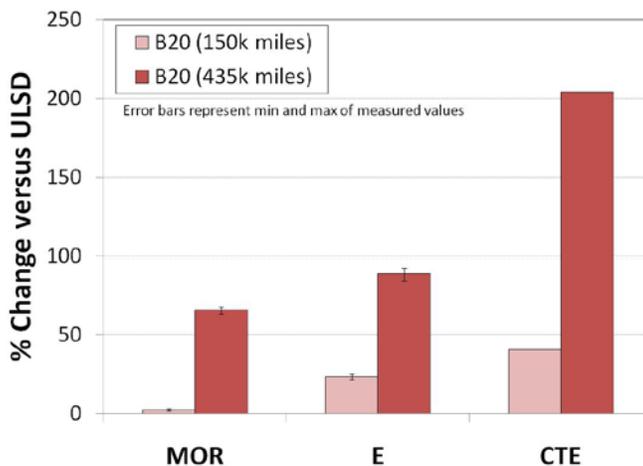


Figure 8. Thermo-mechanical properties of cordierite DPFs outlet section

After exposure to 150,000 miles of biodiesel exhaust, the bend strength for the cordierite DPF was roughly the same across the filter. Compared to the ULSD filter, MOR measurements changed by -5.9%, -9.3%, and +2.1% at the inlet, middle, and outlet sections, respectively. This indicates that the 228 grams of biodiesel ash combined with thermal aging did not significantly impact the strength of the material. The outlet section of the biodiesel filter did have slightly higher elastic modulus (+23.3%) and CTE (+40.5%) compared to the ULSD test filter. While there was a measurable change, the difference was not considered significant given the other possible variables involved in making these measurements. Thus, exposure of the cordierite DPF to 150,000 miles of biodiesel ash did not significantly change the thermal shock resistance characteristics of the material. However, the elemental distribution maps shown in Figure 9 indicate diffusion of the impurity elements into approximately 25-30% of the cell wall thickness of the outlet portion of the DPF.

The DPF aged to 435,000 mile equivalent simulated biodiesel ash loading (without ash cleaning) showed an increase of +65.6% in the bend strength compared to the ULSD test piece. Prior work by Dou and Balland has shown a decrease in cordierite substrate strength as a result of alkali exposure^[1] in contrast to our observation. It is well known that applying a catalyst washcoat to a porous ceramic substrate tends to increase its strength. This results from the inorganic oxide particles in the washcoat filling in some of the porosity of the substrate. One hypothesis for our observation may be that the metal oxide biodiesel ash, deposited as a layer along the length of the channel walls, strengthened the filter substrate analogous to the application of a washcoat. This may have increased the strength to a greater extent than the negative effect of sodium diffusion into the ceramic material. For the 435,000 mile equivalent aged parts the elastic modulus and the CTE were also much higher for the biodiesel test filter, indicating an increase in stiffness and higher thermal expansion characteristics. Although a higher strength tends to increase the thermal shock resistance parameter of a material, the higher elastic modulus and thermal expansion coefficient will lead to a decrease in this parameter. Calculation of the relative thermal shock parameter for the outlet section demonstrates a significant overall decline in this parameter by 69% for the doped B20 exposed filter relative to that exposed to ULSD.

Sections of the outlet portion of the DPF were mounted in epoxy and characterized using an electron microscope and energy dispersive x-ray analysis to observe the extent of diffusion of the alkali and alkaline earth metal impurities from the biodiesel ash into the cell wall of the filter. Figure 9 shows the elemental dot maps for sodium, potassium and calcium across the thickness of the cell wall at the outlet section of the DPF after 150,000 and 435,000 mile equivalent aging. The images represent the cross section of the filter cell wall with the direction of exhaust flow going from right to left. The colors indicate relative concentrations of the elements with dark blue or black being the lowest concentration and red being the highest as indicated on the legend to the right of the images. No attempt was made to quantify the concentration of cations so the colors only provide a means for relative comparison.

In the B20 exposed parts, one sees penetration of all three cations even after 150,000 miles of accelerated aging, however diffusion is only about a third of the way across the wall thickness. A dark blue shade is observed for potassium in the ULSD reference sample, but because there is no concentration gradient and no potassium was present in the fuel we attribute this to background signal. Furthermore the 150,000 mile equivalent aged ULSD cordierite sample was the first test run on the engine before any biodiesel fuel exposure.

The 435,000 mile equivalent aged B20 sample shows diffusion across the entire thickness of the cell wall for all three elements. Some diffusion is also observed in the full-useful-life aged ULSD sample, however since these elements were not present in the fuel we attribute this to cross contamination from upstream components in the exhaust system exposed to biodiesel ash in previous aging cycles.

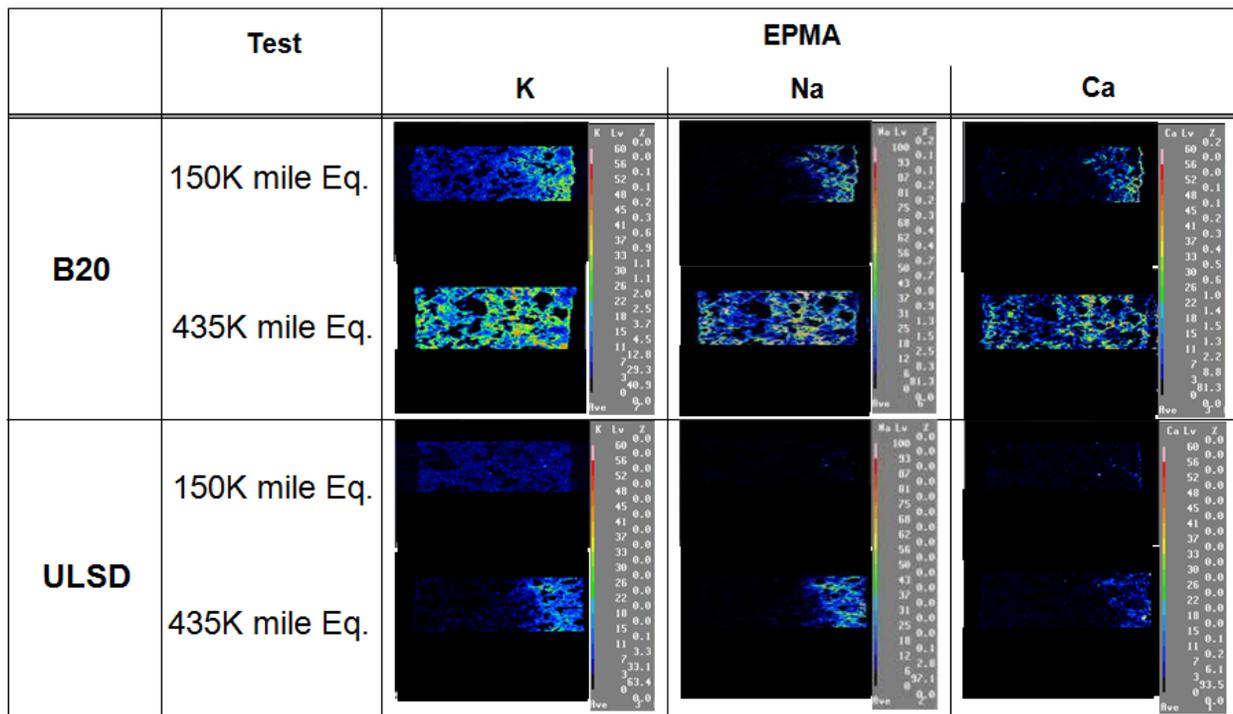


Figure 9. Elemental concentration by SEM-EDX

The SiC and AT DPFs tested to the 150,000 mile equivalent aging were also characterized by the manufacturer. Measurements of MOR, E and CTE were made for the DPFs at the inlet, middle and outlet. The results are shown in Tables 7 and 8. After exposure to 150,000 miles of biodiesel exhaust, all three of the material properties for the SiC DPF were roughly the same across the filter and compared to the ULSD filter changes were small. The outlet of the biodiesel exposed AT DPF showed a slightly higher MOR (+21.1%), a lower CTE (-24.6%) and no change in elastic modulus. While there were measurable differences in the properties of these filters, the difference was not considered significant given the other possible variables involved in making these measurements. Thus, exposure of the SiC and AT DPFs to 150,000 miles of biodiesel ash did not significantly change the thermal shock resistance parameter.

Table 7. Thermo-mechanical properties of B20 SiC DPF (percent change versus ULSD DPF)

	150k mile		
	MOR	E	CTE
inlet	8.7	3.3	2.3
middle	3.9	-3.0	2.3
outlet	6.9	6.5	0.0

Table 8. Thermo-mechanical properties of B20 AT DPF (percent change versus ULSD DPF)

	150k mile		
	MOR	E	CTE
inlet	11.5	-9.1	-20.8
middle	8.8	-20.0	13.0
outlet	21.1	0.0	-24.6

Impact of Biodiesel Ash on DOC Emissions Performance

In this study, the DOC placed upstream of the DPF and operated below 650° C for the 150,000 mile equivalent aging was evaluated. DOC testing and post-mortem analysis were conducted on a MAN D2066 diesel engine. This is a 10.5 L, 325 kW engine certified to the Euro IV emissions standards. HC slip across the DOCs was measured at eight test modes by injecting diesel fuel upstream of the catalysts in a quantity sufficient to achieve a theoretical outlet temperature of 600° C. Operating conditions for the eight-mode test are shown in Table 9 and HC slip is shown in Figure 10.

Table 9. Eight-mode HC slip test operating conditions

Mode	Speed (rpm)	Load (N-m)	DOC temp (C)	DOC SV (1/hr)
1	1980	995	340	120k
2	1570	815	335	70k
3	1255	515	290	40k
4	1770	520	295	65k
5	1900	460	280	40k
6	1950	350	265	40k
7	1980	290	250	65k
8	1360	355	243	39k

A comparison of the two DOCs showed higher HC slip for the biodiesel aged part at all eight modes. Furthermore, the low temperature, low space velocity mode at 243° C showed indications of quenching and increasing HC slip over the duration of that mode. The NO₂ formation from the DOCs was measured across a range of catalyst temperatures. This was done by ramping the engine load from 0 to 100% at a steady-state engine speed of 1100 rpm after a conditioning phase at full load for 30 minutes. The results, shown in Figure 11, demonstrate a significant loss in catalyst NO₂ oxidation activity for the biodiesel aged DOC, reducing the maximum NO₂ formation from about 37% for the ULSD DOC to 21% for the B20 DOC.

The two DOCs were cut apart for optical microscope and chemical analysis. Elevated levels of sodium, potassium, calcium and sulfur were detected with steep concentration gradients from inlet to outlet in the B20 aged parts. All of these components penetrated into the washcoat with a gradient from top to bottom of the washcoat layer. In general the washcoat was in good condition for both DOCs. The exception was the first 1/8th inch of the biodiesel aged part, which showed signs of washcoat cracking most likely due to high sodium levels (> 1 wt% measured by XRF) detected in the front of the DOC. Exposure to biodiesel ash is clearly responsible for the activity loss. Because the bulk of the catalyst washcoat was intact, the loss of catalyst activity was not caused by physical degradation of the washcoat but rather by precious metal poisoning or surface area loss.

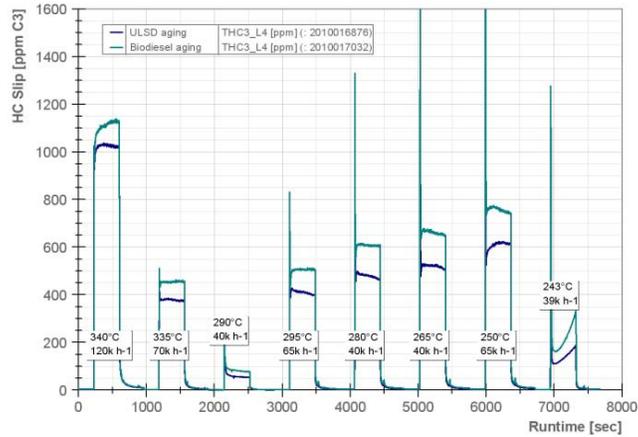


Figure 10. DOC HC slip

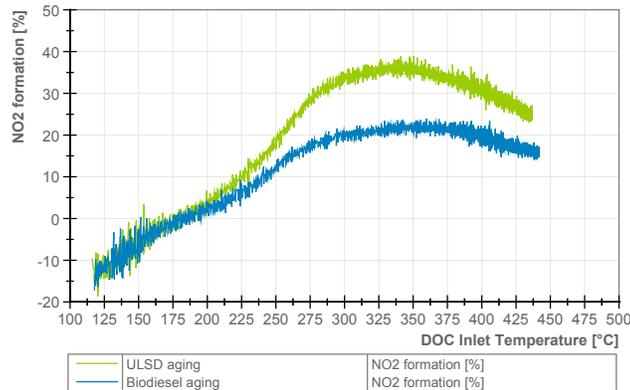


Figure 11. DOC light-off NO₂ formation

Impact of Biodiesel Ash on SCR Emissions Performance

Following the 435,000 mile equivalent aging in tests 4a and 4b, the SCR catalysts were evaluated on a 2008 Cummins ISC. This is an 8.3 L, 223 kW engine that also incorporated a DOC and DPF upstream of the aged SCR bricks. The DOC/DPF were not the same as those used in the aging study, but were representative of current production catalysts that had been aged independently prior to the evaluation tests. The aging consisted of 50 hrs continuous active regeneration with fuel injected up-stream of the DOC (400° C, inlet) to produce 650° C at the inlet of the DPF. A urea injection system and the 435,000 mile equivalent aged SCR catalysts were then mounted down-stream of the DPF. The SCR system consisted of two catalyst bricks placed in series and are described as SCR₁ and SCR₂. SCR catalyst performance was evaluated over the heavy-duty diesel transient (HDDT) test cycle, following the hot-start federal test procedure. All emission testing was conducted with ULSD as the test fuel. The SCR catalyst temperature range over the HDDT cycle was 202° to 305° C and peak SCR space velocity was 65,000 hr⁻¹. Emission measurements were made using three matched FTIRs to simultaneously measure exhaust emissions at SCR-in, SCR₁-out and SCR₂-out locations. Results reported at the SCR₂-out location are cumulative for both bricks. Urea solution was injected into the exhaust at an NH₃ to NOx molar ratio (α) of 1.0, based on the NOx measured at the SCR-in location.

Percent reduction in NOx emissions averaged for three hot-start repeats of the HDDT test cycle are shown in Figure 12. As can be seen, the majority of the NOx conversion was achieved over SCR₁ with some additional NOx reduction over SCR₂. The SCR catalysts aged with ULSD achieved NOx conversion levels of 85.7% after SCR₁ and 92.1% after the second SCR brick (SCR₂). The SCR catalysts aged with biodiesel showed lower NOx

performance with only 78.0% conversion at SCR₁-out and 87.2% NO_x conversion at the SCR₂-out locations, indicating catalyst deactivation due to the biodiesel aging.

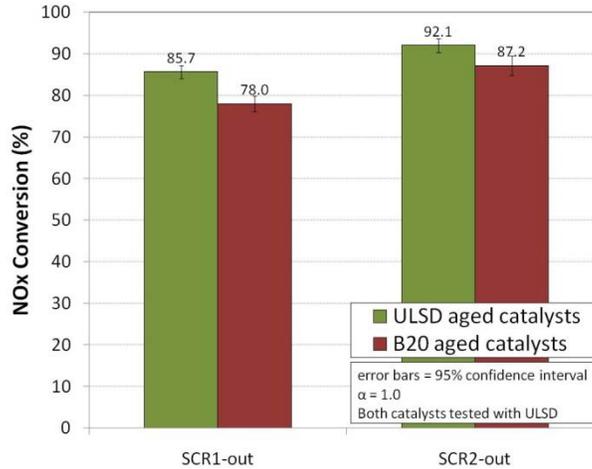


Figure 12. Averaged NO_x conversion of aged SCR catalysts

The brake specific engine-out NO_x produced over the hot-start HDDTs and measured at the inlet of the SCR averaged 1.83 and 1.68 g/bhp-hr. These data, along with SCR₁-out and SCR₂-out brake specific NO_x levels for the aged SCR catalysts are shown in Figure 13. This shows that the SCR catalysts aged on ULSD resulted in NO_x levels of 0.15 g/bhp-hr at the tailpipe location (SCR₂-out), which is comfortably below the 0.20 g/bhp-hr 2010 on-highway EPA emission standard. The SCR catalysts aged on biodiesel however, resulted in a higher 0.22 g/bhp-hr NO_x level, which is slightly above the emission limit. It is important to note that these tests represent only the hot portion of the weighted FTP test cycle.

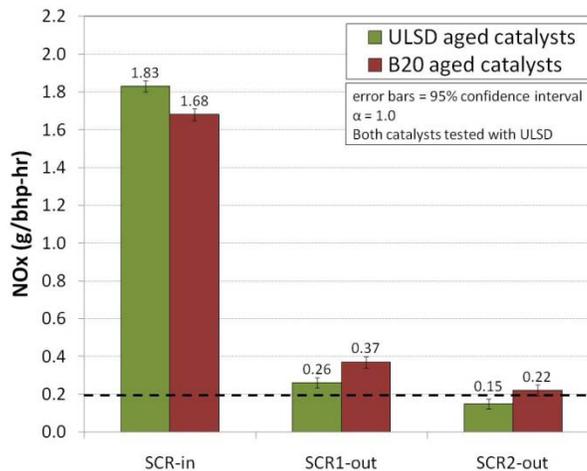


Figure 13. Averaged brake specific NO_x measurements over the heavy-duty transient cycle

The cycle cumulative NH₃ slip levels are compared in Figure 14 for the two sets of aged SCR catalysts. These levels are for the third of the three HDDT cycles which gave the highest level of slip. As might be expected, the NH₃ slip level at SCR₁-out was higher than at SCR₂-out location. The cycle cumulative NH₃ slip for the SCR catalysts aged with ULSD fuel was 1.09 grams. The peak NH₃ slip over the HDDT cycle was approximately 50 ppm, which can be easily controlled with a down-stream ammonia oxidation catalyst to below the target 20 ppm maximum. The NH₃ slip for the SCR catalysts aged with biodiesel was slightly lower at 0.82 grams.

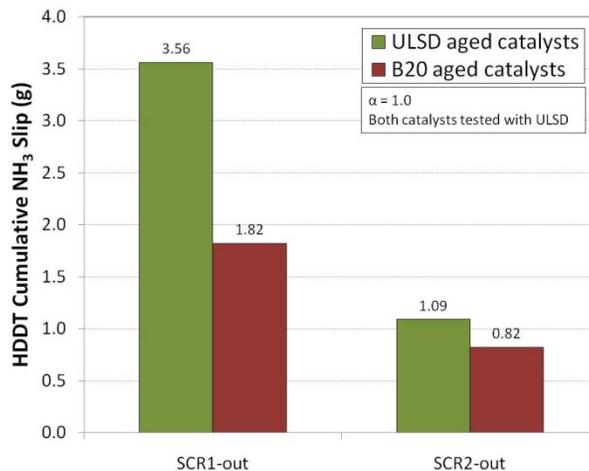


Figure 14. Cumulative ammonia slip measurements for the third transient test

While further evaluation and postmortem analysis of the aged SCR catalysts is necessary to determine the cause of the observed deactivation, some aspects can be discussed now. Table 10 shows the thermal history of the ULSD and B20 aged catalysts. The ULSD aged catalyst experienced greater time at temperatures above 550°C, so greater thermal deactivation is not likely to be responsible for the lower activity of the B20 aged catalyst. Because ash particles are very effectively trapped by the DPF, if metals are responsible for the deactivation it is likely because some ash compounds, especially alkali metal compounds, can sublime at the high temperature DPF regeneration conditions and be transported to the SCR. Ongoing studies will evaluate the composition of the ash collected in the DPF, and model the vapor pressure of the various ash species. It is apparent that at 850°C the volatility of potassium salts is higher than that of the corresponding sodium salts, and there is more potassium in the vapor phase at equilibrium. A reasonable hypothesis is that potassium in the form of hydroxide and sulfate is vaporized from the DPF and transported to the SCR catalyst where it causes deactivation. Examination of this hypothesis will be the subject of future work.

Table 10. SCR Thermal Exposure

	Units	ULSD	B20
SCR T (avg)	°C	458.2	453.4
<500°C	hours	74.8	77.1
500°C to 525°C	hours	2.6	16.8
525°C to 550°C	hours	139.7	135.4
550°C to 575°C	hours	16.7	7.4
575°C to 600°C	hours	1.2	0.1

SUMMARY/CONCLUSIONS

- An accelerated aging test method was developed to expose exhaust emission control components to biodiesel ash and thermal aging using a heavy-duty engine. The biodiesel was doped with alkali and alkaline earth impurities to represent the upper limit of these impurities as allowed by ASTM D6751.
- The impact of long-term biodiesel ash exposure was investigated for three different DPF substrate types (cordierite, AT, and SiC), as well as for DOC and SCR catalysts.
- It is important to note that while the ash exposure from the biodiesel was accelerated, the ash exposure from the engine lube-oil was not. However, the lube-oil ash contribution would be the same regardless of fuel type. The amount of thermal aging is also the same for each fuel. Thus, for this study, comparisons of the ULSD and B20 test parts at the 150,000 and 435,000 mile equivalent test intervals represent the same amount of thermal aging and lube-oil ash exposure with the only difference being the additional ash that would be seen by using biodiesel.
- DPF and DOC parts were aged to a 150,000 mile equivalent operation, which is the EPA's minimum ash-clean interval for a DPF. In addition a pair of cordierite DPFs and SCR catalysts were aged to a 435,000 mile equivalent operation, which is the EPA's required full-useful-life durability limit for heavy heavy-duty applications.
- Estimates of DPF pressure drop indicate that the additional ash exposure from 150,000 miles of operation with B20 will result in a 6.8% increase in backpressure.
- The catalytic activity of a DOC exposed to 150,000 mile equivalent aging of biodiesel ash was reduced for both HC and NO₂ oxidation. Engine tests showed some drop of heat-up performance of the B20 aged DOC compared to its ULSD aged counterpart, and furthermore, NO₂ formation activity was reduced approximately 30% compared to the ULSD aged DOC.
- The mechanical durability of the cordierite, SiC and AT DPFs after 150,000 mile equivalent operation was measured. The changes in bend strength, elastic modulus and coefficient of thermal expansion were determined to be comparable for the ULSD and B20 aged parts.
- The mechanical durability of the cordierite DPFs aged to 435,000 mile equivalent operation with biodiesel (with no ash cleaning) showed an increase in strength as well as an increase in elastic modulus and CTE. Overall the relative thermal shock resistance parameter declined by 69% compared to the ULSD test filter indicating a greater susceptibility to thermal shock.
- Although it was downstream of the DPF, the SCR catalyst was impacted by the biodiesel fuel aging. The NO_x conversion showed activity loss of 5% over the hot start HDDT test cycle and emissions from the biodiesel aged SCR system were slightly above the 0.20 g/bhp-hr standard.
- It should also be noted that the biodiesel test fuel was additized with both alkali and alkaline earth metals. Thus it cannot be determined which of these biodiesel impurities was the cause of any decline in performance. However, because calcium ash is a normal component found in lube oil ash, and magnesium is a component of cordierite, it is believed that the alkali metals sodium and potassium were primarily responsible for the chemical effects observed here.
- The results of this study suggest that long term operation with B20 at the current specification limits for alkali and alkaline earth metal impurities can adversely impact the performance of DOC, DPF and SCR systems.

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DEFINITIONS/ABBREVIATIONS

°C	degrees Celsius
ASTM	ASTM International
AT	aluminum titanate
Ca	calcium
cm	centimeter
CO	carbon monoxide
CTE	coefficient of thermal expansion
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
E	elastic modulus
EPA	U.S. Environmental Protection Agency
g/L	gram per liter
gal	gallon
HC	hydrocarbons
HDDT	heavy-duty diesel transient
K	potassium
kg	kilogram
Mg	magnesium
mm	millimeter
MOR	modulus of rupture
mpg	miles per gallon
Na	sodium
NH ₃	ammonia
N-m	Newton-meter
NO ₂	nitrogen dioxide
NO _x	oxides of nitrogen
NREL	National Renewable Energy Laboratory
ppm	parts per million
rpm	revolutions per minute
SCR	selective catalytic reduction
SiC	silicon carbide
ULSD	ultra-low sulfur diesel
wt%	weight percent

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