

Evaluation of Fuel-Borne Sodium Effects on a DOC-DPF-SCR Heavy-Duty Engine Emission Control System: Simulation of Full-Useful Life

Michael Lance, Andrew Wereszczak, and Todd J. Toops
Oak Ridge National Laboratory

Richard Ancimer, Hongmei An, Junhui Li, and Leigh Rogoski
Cummins Inc

Petr Sindler, Aaron Williams, Adam Ragatz, and Robert L. McCormick
National Renewable Energy Laboratory

ABSTRACT

For renewable fuels to displace petroleum, they must be compatible with emissions control devices. Pure biodiesel contains up to 5 ppm Na + K and 5 ppm Ca + Mg metals, which have the potential to degrade diesel emissions control systems. This study aims to address these concerns, identify deactivation mechanisms, and determine if a lower limit is needed. Accelerated aging of a production exhaust system was conducted on an engine test stand over 1001 h using 20% biodiesel blended into ultra-low sulfur diesel (B20) doped with 14 ppm Na. This Na level is equivalent to exposure to Na at the uppermost expected B100 value in a B20 blend for the system full-useful life. During the study, NO_x emissions exceeded the engine certification limit of 0.33 g/bhp-hr before the 435,000-mile requirement. Replacing aged diesel oxidation catalyst (DOC), diesel particulate filter (DPF), and selective catalytic reduction (SCR) devices with new degreened parts showed that each device contributed equally to the NO_x increase. Following this systems-based evaluation, a detailed investigation of the individual components was completed. Na was determined to have minimal impact on DOC activity. For this system, it is estimated that B20-Na resulted in 50% more ash into the DPF. However, the Na did not diffuse into the cordierite DPF nor degrade its mechanical properties. The SCR degradation was found to be caused by a small amount of precious group metals (PGM) contamination that increased NH₃ oxidation, and lowered NO_x reduction. Therefore, it was determined that the primary effect of Na in this study is through increased ash in the DPF rather than deactivation of the catalytic activity.

CITATION: Lance, M., Wereszczak, A., Toops, T., Ancimer, R. et al., "Evaluation of Fuel-Borne Sodium Effects on a DOC-DPF-SCR Heavy-Duty Engine Emission Control System: Simulation of Full-Useful Life," *SAE Int. J. Fuels Lubr.* 9(3):2016, doi:10.4271/2016-01-2322.

INTRODUCTION

Alkali and alkaline earth metals can potentially enter diesel fuel from refinery salt driers, tank water bottoms, pipeline corrosion inhibitors, or seawater used as tanker ballast. Biodiesel (fatty acid methyl esters) is another potential source because sodium (Na) or potassium (K) methoxide catalyzes the reaction of vegetable oils with methanol to form methyl esters. Residual amounts of Na or K can remain in the biodiesel, and small amounts of calcium (Ca) or magnesium (Mg) can also contaminate the biodiesel from the purification process [1, 2]. Both Na + K and Ca + Mg are limited to no more than 5 ppm in ASTM D6751 "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels" [3]. These metal contaminants can form an inorganic ash consisting of oxides, sulfates, hydroxides, or carbonates in the combustion process, which is then deposited onto the exhaust emission control devices. Alkali metals are well known to poison certain catalysts and can impact the mechanical properties of ceramic substrates [4, 5]. Furthermore,

alkali metal hydroxides are volatile in the presence of steam and can penetrate the catalyst washcoat or substrate or potentially move from one emission control system component to another.

Research has examined long-term durability impacts of biodiesel on emission control systems. Engine dynamometer testing that simulated 120,000 miles of use in a light-duty car showed no negative impacts on diesel particulate filter (DPF) or oxides of nitrogen (NO_x) adsorber catalyst durability for a commercial biodiesel (B20 blend) [6]. Similar testing of a urea selective catalytic reduction (SCR) catalyst demonstrated no catalyst activity loss in comparison to conventional diesel, although both the diesel and B20-exposed systems experienced a relatively high degree of catalyst deactivation such that the vehicle would not have been able to meet the Tier 2 Bin 5 emission standards at end of test [7]. Subsequent studies examined the impact of residual metals (Na, K, Mg, and Ca) that can be present in biodiesel and how these metals might impact catalyst durability. In a follow-up study the emission control system on a Ford F250 truck

was exposed to the equivalent of 150,000 miles of a biodiesel (B20) exhaust containing Na, K, or Ca [8]. The system included a diesel oxidation catalyst (DOC), a urea SCR catalyst, and a DPF mounted on the engine in that order. Over the course of the catalyst aging, no activity loss or increase in emissions from the truck was observed. However, detailed investigation of the fate of the metals on the catalysts and the activity at different locations in the catalyst parts showed significant impact. Bench flow reactor experiments conducted on samples taken from aged SCR catalysts showed that parts exposed to Na and K (the first few centimeters of the catalyst monolith) had reduced activity. Bench flow reactor and electron probe microanalysis (EPMA) of the DOCs also showed signs of deactivation for parts exposed to Na and K. These results imply that heavy-duty truck systems with longer lifetimes and exposure to larger volume of exhaust may prove more sensitive to these contaminants. The metals-aging study accelerated catalyst exposure by doping of the fuel with high levels of metal. A related study investigated the possibility that this approach to accelerated aging created deactivation modes that would not be observed at normal fuel metal levels [9]. Results showed that beyond a certain threshold, the acceleration rate creates an artificial mechanism for catalyst deactivation.

Research has also examined the impact of biodiesel metals on heavy-duty catalyst system deactivation. Fuel doped with high levels of biodiesel metals was burned in an engine and used to expose heavy-duty catalyst parts to the equivalent of 435,000 miles of metals [10]. The system consisted of a DOC, DPF, and urea SCR mounted on the engine in that order. No evidence of SCR catalyst deactivation was observed, but some degradation of DOC activity and of DPF thermal shock resistance was observed. However, at the time this study was conducted, heavy-duty emission control systems were in development and not yet commercially available. Engine and catalyst manufacturers anticipated that occasional temperature excursions to 850°C could occur, and a fraction of catalyst aging time was spent at this very high temperature. After introduction of these systems into the market in 2010, manufacturers determined that temperatures above 650°C were rarely if ever encountered. Thus, the catalyst and filter degradation observed in this study may have been an artifact of the very high temperatures utilized.

The research described in this paper utilized accelerated catalyst deactivation to determine the impact of Na on a commercial 2010 emissions-compliant emission control system operated to simulated full-useful-life (FUL)-equivalent fuel exposure. Results indicate that the only adverse impact of Na was on the total ash loading in the DPF.

METHODS

Catalyst Aging

A full production exhaust system from a 2010 Cummins ISL engine was subjected to accelerated aging. The aftertreatment devices from front to back were a DOC, DPF, SCR, and an ammonia slip catalyst (ASC). The size, cordierite substrate cell density, and wash coat compositions for all four devices are listed in Table 1. Two identical exhaust systems were acquired, one to serve as a baseline and the second for accelerated aging. These parts were degreased on the 2010

Cummins ISL engine using a 4 h proprietary break-in cycle followed by five hot-start Federal Test Procedure (FTP) cycles and six software-forced DPF regenerations.

Table 1. Catalyst specifications.

Test Piece	D x L (in.)	Cells/in2	Wash Coat
DOC	10.5 x 4	400	Pt:Al ₂ O ₃
DPF	10.5 x 12	200	Pt/Pd:Al ₂ O ₃
SCR	10.5 x 6	400	Cu:SAPO-34
ASC	10.5 x 4	400	Fe Zeolite / Pt:Al ₂ O ₃

Catalyst aging was conducted using a Caterpillar C9 ACERT engine in a dynamometer test cell at SGS-ETC in Denver, Colorado. FTP emissions evaluation was performed on the 2010 Cummins ISL at the National Renewable Energy Laboratory's Renewable Fuels and Lubricants Laboratory in a dynamometer test cell conforming to the requirements of the Code of Federal Regulations Title 40, part 86, subpart N. Engine intake air temperature, pressure, and humidity were controlled. NO_x emissions were measured by chemiluminescence, CO and CO₂ by nondispersive infrared, and unburned hydrocarbon by continuous flame ionization detector.

The engine and emission control system configuration is shown in Figure 1. Note that the Cummins engine was never operated on B20 or Na-doped fuel during this test program. Temperature and pressure were monitored at the outlet of each aftertreatment device.

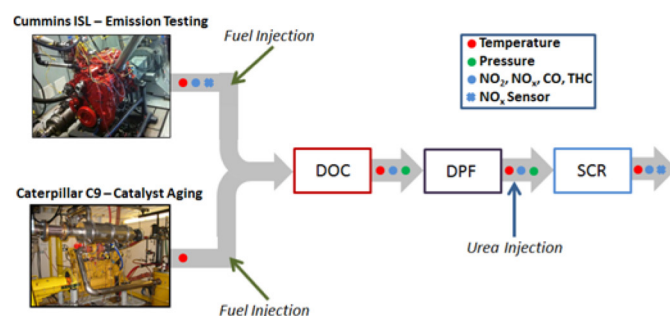


Figure 1. Catalyst aging and emission testing configuration.

The aging fuel was B20 doped with 14 ppm Na in the form of diethyl sulfosuccinate sodium salt, which resulted in 14 times the effective ASTM limit (based on a B100 limit of 5 ppm Na). To reach FUL of 435,000 miles, a line haul truck with a fuel economy of 6 mpg requires 72,500 gallons of B20 (435,000 miles/6.0 mpg). Dividing this volume by 14 gives 5,179 gallons of B20 doped with 14 ppm Na to reach the FUL-equivalent Na exposure. The actual amount of fuel burned was 5,381 gallons, which is within 4% of the target amount. The lubricant (Chevron Delo LE SAE 15W-40) was changed at 250 h intervals, and oil consumption was quantified by weighing the oil before and after each oil drain interval.



FUL was simulated in 1001 h following the three-mode 65-min aging cycle shown in [Figure 2](#). Each cycle included a 25-min hold at a DOC outlet temperature of 260°C and DOC space velocity (SV) of 63K h⁻¹, a 25-min hold at 380°C and a DOC SV of 133K h⁻¹, and a 15-min ramp and hold at 550°C and a DOC SV of 89K h⁻¹. Once every 5 cycles, a high temperature spike to 600°C for 200 s was included to simulate a temperature excursion during DPF regeneration. This aging cycle does not allow buildup of a normal soot cake, but simulates exposure to high temperatures for times that equate to FUL. This protocol was repeated 923 cycles, resulting in 179 h spent above 550°C. Urea was injected during the entire aging process with a target ammonia-NO_x ratio (ANR) of 1.0. The stock Cummins urea injector was removed and replaced with an independent injector during aging. This injector began to fail in the final 100 h of aging, and was not operational in the final 24 h although this is not expected to impact the results. Urea was not injected during startup when temperatures were below 250°C to avoid the possibility of urea deposit formation.

The DPF was weighed approximately every 50 h to quantify ash loading following the high temperature portion of the cycle to remove any soot. Composite FTP emissions testing using the Cummins ISL engine was performed at 0, 280, 553, 756, and 1001 h. The preconditioning and test sequence for the composite FTP emission tests was the following:

- Active DPF regeneration for 20 min at approximately 1700 rpm/720 ft-lb torque
- A series of ANR sweeps at different steady-state modes (not reported here)
- Five warm FTPs with a 20-min soak interval
- Minimum 10 h cold soak
- Cold start FTP followed by a 20-min soak
- Five warm FTPs at 20-min intervals to generate emissions data.

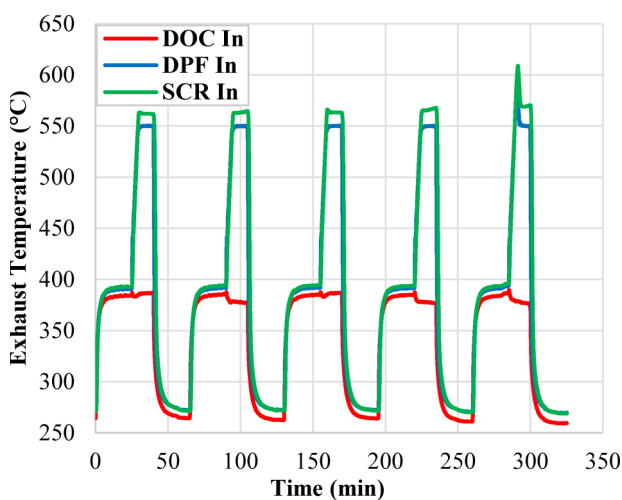


Figure 2. A 5-cycle portion of the aging protocol.

After completion of the composite FTP, 25-mm long x 6-mm diameter micro-cores were extracted from the front face of the DOC and SCR for materials analysis and bench reactor testing. Additional samples were taken from the 1001-h-aged DOC and SCR at different

axial and radial locations. After aging was completed, hot-start FTP testing was conducted to assess the contributions of the DOC, DPF, and SCR to changes in the aftertreatment system performance by systematically swapping aged for degreened components.

Post-aging Catalyst Analysis

Bench reactor testing was performed on micro-cores extracted from the DOC and SCR during the aging protocol to assess catalyst degradation. Micro-cores from the inlet and outlet of the fully aged DOC were treated following the protocols listed in [Table 2](#) to isolate the effects that different contaminants had on the DOC performance. Following each treatment, the NO₂ to NO_x ratio was evaluated following the conditions listed in the last row of [Table 2](#). Additional details on the methodology can be found in Ref [11].

The micro-cores from the SCR catalysts were characterized using the Cummins four-step reactor protocol [13]. The samples were tested as-received and with pre-treatment at 1 h at 500°C, and 2 h at 700°C to probe the effect of different aging mechanisms.

Following aging, small samples of the DOC, DPF, and SCR were metallographically sectioned, polished, and examined by scanning electron microscopy and EPMA using a JEOL Model 8200 microprobe. Samples for scanning transmission electron microscopy (STEM) were extracted from some of the mounted specimens using a Hitachi NB-5000 dual beam focused-ion beam. High-resolution elemental mapping and imaging of individual PGM particles was collected using a FEI Talos F200X STEM.

Table 2. Contaminant removal and NO oxidation evaluation protocols [12].

Treatment	Conditions	Purpose
1 h at 500 °C	60 k/h, 10% O ₂ +7% H ₂ O+Ar, 500°C:1 h	Removal of adsorbed HC, H ₂ O, etc.
Rich de-sulfation	600°C; 5 min rich→5 min lean→5 min rich→5 min lean Lean: 10% O ₂ + 7% H ₂ O + Ar Rich: 1% H ₂ +7% H ₂ O + Ar	Remove S bound with PGM or supporting materials
De-ionized water wash	Four cycles of de-ionized water washing Ultrasound, 70°C, 15 min each cycle	Remove water-soluble contaminants
Acid wash	One cycle of acid washing organic acid mixture, ultrasound, 70°C 1 h.	Removal of all contaminants
NO oxidation evaluation	200 ppm NO+ 10% O ₂ +7% H ₂ O + Ar, 60 k/h 150 °C→450°C by 50°C increment	Performance evaluation

The maximum apparent biaxial failure stress of the DPF was determined by machining 25 tiles that were 108 mm square and 6 mm thick from a fresh DPF and the fully aged DPF. The tiles were loaded using a ring-on-ring biaxial loading fixture, and the load displacement curve was measured. Unlike previous DPF testing, which estimated the fracture strength of the cordierite substrate by accounting for the cellular geometry of the DPF using finite element analysis [8, 14], only the maximum apparent biaxial failure stress of the cellular structure was measured, which still allows for a quantitative comparison of any changes in the DPF strength before and after aging. The coefficients of thermal expansion (CTEs) versus temperature of the fresh and aged DPF were measured using a dual-rod dilatometer. Similar to previous work [8], the CTE specimens were 3 by 3 DPF channels square and 25.4 mm in length and were loaded along the DPF flow direction.

RESULTS AND DISCUSSION

Engine Emissions Testing

The NO_x emissions measured using the FTP composite test on the Cummins ISL engine are shown in Figure 3. The FUL NO_x limit of 0.33 g/bhp-hr for this engine was reached before the 435,000-mile-equivalent aging was completed. This limit was exceeded about halfway into the test. This result was unexpected because Na-containing compounds should theoretically be in the form of particles that are trapped by the DPF prior to reaching the SCR. In addition, the DPF backpressure increased continuously as the test progressed. The high DPF backpressure triggered the controller to initiate more frequent DPF regenerations, making it difficult to complete the composite FTP test. Ash cleaning was conducted at 756 h and again at the completion of aging to enable uninterrupted emission testing.

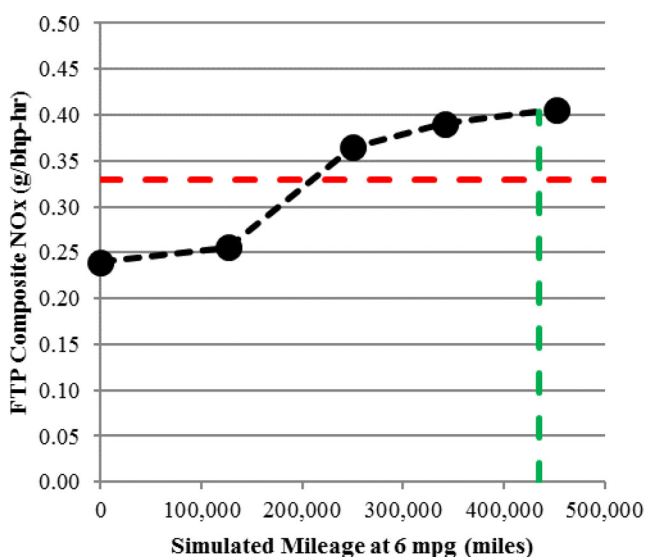


Figure 3. NO_x emissions test results. The red line indicates the FUL NO_x limit of 0.33 g/bhp-hr, and the green line is the FUL limit of 435,000 miles.

Prior to sectioning the catalysts, hot-start FTP emissions testing was conducted to assess individual component contributions to the total system degradation by systematically swapping aged for degreened components. The test results from these combinations are shown in Figure 4. Because these were hot-start FTP tests, the results cannot be

directly compared to the composite FTP results in Figure 3, but they can be compared to one another. Consistent with the results in Figure 3, the hot-start FTP NO_x emissions increase from the original degreened system (first bar) to the fully aged system (second bar). The third, fourth and fifth bars in Figure 4 correspond to the NO_x emissions after replacing degreened parts for aged DOC, DPF, and SCR parts, respectively. The NO_x emissions recovered about equally for all three cases, suggesting that the three components contribute about the same amount to the total system degradation for NO_x. The configuration associated with the sixth bar was tested to isolate the effect of degraded SCR from the effect of degraded NO oxidation due to the aged DOC and DPF. The fact that the height of the sixth bar lies half way between that of the degreened and fully aged systems provides further evidence that the SCR performance degraded during the test. Finally, to ensure that the engine and dosing system had not changed from the original evaluation, the full degreened system (the seventh bar in Figure 4) was tested, and a result similar to the original degreened system was obtained. These results show that all the component aftertreatment devices were impacted by the aging, but it is not clear from this systems-level test whether or not the degradation is due to Na, or what the degradation mechanisms are for each individual component. Further analysis using bench reactor testing and materials characterization on the individual aftertreatment components were carried out and are discussed in the next sections.

DOC Postmortem Analysis

Figure 5 shows the NO₂ to NO_x ratio from 150° to 450°C measured on micro-cores extracted from the front face of the DOC during aging. The NO oxidation first rises and then falls with continued aging. Previous studies have shown that NO oxidation performance improves as the Pt sinters and particle size increases with hydrothermal aging [15]. However, sintering of the Pt also reduces the number of active sites. During the early stages of the aging process, the benefit of larger particle sizes is expected to offset the loss in active sites, leading to a net improvement in NO oxidation performance. This result is consistent with the higher NO₂ to NO_x ratios observed as the DOC ages over the 0 to 280 h time period (see Figure 5). However, further aging eventually leads to a point in which the loss in active sites outweighs the benefits of larger Pt particle size, resulting in a net decrease of the NO oxidation, again consistent with the findings in this study, where the NO₂ to NO_x ratios decrease after 280 h. The accumulation of chemical contamination would also be expected to further contribute to the deactivation of the DOC, particularly near the inlet [12].

To characterize the presence of contaminants on the DOC, the elemental composition on the surface of the micro-cores was measured using energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope. Measurements (not shown) indicate that the Na concentration on inlet micro-cores increased and then stabilized with aging time. Fully aged micro-cores from the middle and outlet also showed Na on the surface, but at somewhat lower concentrations than at the inlet. Phosphorus and sulfur were also detected on the cores at levels within the normal range of field-returned parts with similar operating times. In addition, it was observed that the outer 50-mm wide annulus of the DOC (the part that was coated with a Na-Ca sulfate powder) that penetrated ~1 mm into