

Post Mortem of an Aged Tier 2 Light-Duty Diesel Truck Aftertreatment System

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ABSTRACT

A 2005 prototype diesel aftertreatment system consisting of diesel oxidation catalysts (DOC), Cu/zeolite Selective Catalytic Reduction (SCR) catalyst, and Catalyzed Diesel Particulate Filter (CDPF) was aged to an equivalent of 120k mi on an engine dynamometer using an aging cycle that incorporated both city and highway driving modes. The program demonstrated durable reduction in particulate matter (PM) and nitrogen oxides (NO_x) emissions to federal Tier 2 levels on a 6000 lbs light-duty truck application. Very low sulfur diesel fuel (~15 ppm) enabled lower PM emissions, reduced the fuel penalty associated with the emission control system, and improved long-term system durability. A total of 643 filter regenerations occurred during the aging that raised the entire catalyst system to high temperatures on a regular basis. After testing the aged system on a 6000 lbs light-duty diesel truck, a post mortem analysis was completed on core samples taken from the DOC, SCR catalyst, and filter. It was found that the outlet of the DOC and the inlet of the SCR were deteriorated most significantly. Known catalyst poisons such as P were found in the DOC and SCR washcoats. The filter contained residual ash that was composed mainly of Ca, P and Zn compounds. The inlet of the SCR catalyst contained Pt that degraded the NO_x conversion in that portion of the catalyst. Overall, the system was still quite functional and delivered 74% NO_x conversion on the U.S. Federal Test Procedure (FTP-75) for light-duty vehicles.

INTRODUCTION

Light-duty diesel vehicles sold today must meet U.S. Tier 2 and California LEV II emission standards. The durability requirement of 120k mi for the aftertreatment system is challenging. Choices for the 90+% NO_x

conversion needed for most diesels to comply with the emission standards include 1) lean NO_x traps and 2) selective catalytic reduction (SCR) with an ammonia-based reductant such as aqueous urea. SCR systems typically have a cost advantage over LNT systems for engine displacements above about 2-2.5L [1]. Base metal/zeolite SCR catalysts containing Fe or Cu appear to have an advantage over traditional vanadia-based formulations, which lack the thermal durability required to survive filter regenerations [2]. Zeolite-based catalysts have not been widely used on vehicles; rather, they have typically been used at stationary sources where conditions such as temperature and flow rate do not vary widely and rapidly as they do on vehicles [3]. An aftertreatment system containing a DOC, Cu/zeolite SCR catalyst, and CDPF was aged for 2500 h on an engine dynamometer using a mid-size diesel engine designed for a light-duty truck application. An aging cycle was used that included both city and highway driving modes to simulate 120k mi. A total of 643 filter regenerations occurred during the aging that raised the DOC to a temperature of about 800°C and the SCR catalyst to at least 600°C on a regular basis [4-5].

A post mortem analysis of the catalysts followed the aging. After the system performance was evaluated on a 6000 lbs light duty diesel truck, the chemical and physical properties of each catalyst were studied in detail, resulting in valuable information on aging processes of lean diesel catalyst systems.

EXPERIMENTAL

CATALYST SYSTEM AGING - The aftertreatment system (Figure 1) was aged 2500 hours using a mid-size prototype diesel engine on a dynamometer. This was equivalent to a total mileage of 120k mi using a Ford

corporate drive cycle that incorporated both city and highway driving modes (Figure 2). The average vehicle speed was 47 mph, with a peak speed of 75 mph. There were two DOCs located in the downpipe just after the turbocharger, and a larger DOC located underbody. A solution of 32.5 wt% urea in water was sprayed against the exhaust flow with atomizing air, and a spray target ensured adequate distribution of the urea in the exhaust gas. The flow rate of urea was controlled based on fuel flow and information from a catalyst inlet temperature sensor, an air meter, and a NOx sensor. A Cu/zeolite SCR catalyst and a catalyzed DPF followed. All catalyst components were obtained from major automotive suppliers, with physical details noted in Table 1.

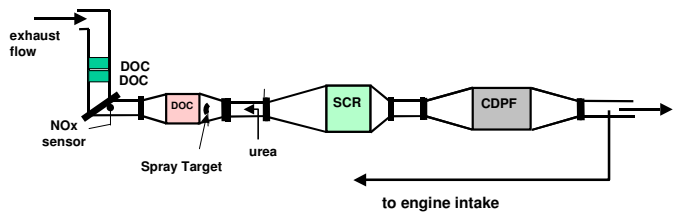


Figure 1. Exhaust system configuration for a mid-size prototype diesel engine on a 6000 lbs light-duty truck.

Table 1
Catalyst Descriptions

Catalyst Type	Substrate type	Active Component(s)
DOC (downpipe)	Stainless Steel	Pt
DOC (underbody)	Cordierite	Pt
SCR Catalyst	Cordierite	Cu/zeolite
CDPF	SiC	Pt

The filter was regenerated a total of 643 times, with each regeneration typically lasting ten minutes, including six minutes with the SCR catalyst at high temperature. In all, the catalysts spent approximately 64 h at high temperatures in excess of 600 °C.

Ultra low sulfur (<15 ppm S) diesel fuel was obtained from ExxonMobil. The fuel properties shown in Table 2 met the EPA certification fuel standards for 2007. The engine oil was Texaco Ursa Super Plus with properties shown in Table 3.

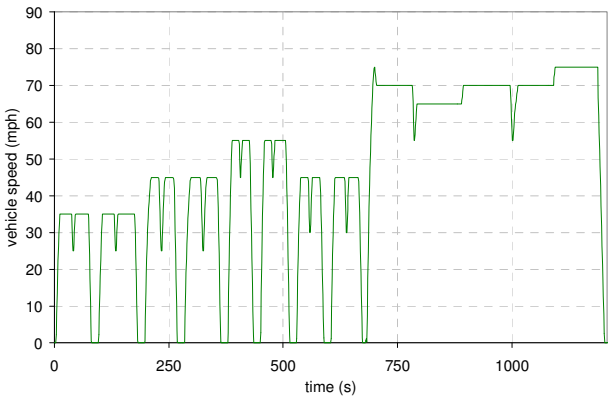


Figure 2. Vehicle speed trace for the aging cycle.

Table 2
Program Fuel Properties

Sulfur, ppm	12.5
Density, kg/m ³	841.1
Aromatics, vol%	29.5
Polyaromatics, wt%	11.0
Cetane number	44.9
T50, °C	249
T90, °C	307

VEHICLE TESTING - The aged aftertreatment system was tested on a 6000 lbs light-duty truck (LDT) with the same type of mid-size prototype diesel engine as used on the engine dynamometer. The vehicle was tested at the Vehicle Emissions Research Laboratory (VERL) located within Ford Research & Advanced Engineering. Four bench/analyzer systems (HC, CO, NOx, and CO₂) were available, as well as a mass spectrometer and two FTIR instruments for real-time emissions analysis, a gas chromatograph for off-line analysis, and balance equipment for particulate filter weighing. The FTIR instruments were used to measure non-regulated emissions such as NH₃ and N₂O. VERL also had a temperature and humidity controlled soak area nearby for vehicle preconditioning.

Table 3
Program Lube Oil Properties
(Texaco Ursa Super Plus)

SAE Grade	10W-30
CPS Number	222120
MSDS Number	8604
API Gravity	30.4
Viscosity	---
cSt @ 40 °C	79.1
cSt @ 100 °C	11.1
Viscosity, Cold Crank, °C/Poise	-25
Viscosity Index	129
Flash Point, °C	230
Pour Point, °C	-42
Sulfated Ash, wt%	1.18
Base Number, ASTM D 2896	9.2
Phosphorus, wt%	0.114
Zinc, wt%	0.127

X-RAY OF CDPF ASSEMBLY - After aging, the filter was removed from the exhaust system and photographed using a high resolution X-ray machine to determine if the substrate was physically cracked or damaged and then the entire assembly was inspected for defects. X-ray scans were taken every 10 mm starting from the outer skin and scanning radial to depict the channel length. Multiple scans were taken throughout the filter in order to see the entire profile.

SURFACE AREA MEASUREMENT - Surface area analysis was performed using the Micromeritics ASAP 2400 in conjunction with a custom built set of glassware that is capable of performing the analysis on an intact core up to one inch diameter and one inch in length. Data are reported as BET surface areas.

XRF AND XRD ANALYSES - X-ray fluorescence (XRF) specimens were prepared by first grinding each 1-inch diameter by 1-inch long core sample in a ceramic-lined grinding dish to obtain a fine, homogenous powder. A 6-gram sample of each powder was then mixed with 0.5 grams of Chemplex® X-Ray Mix, packed into an

aluminum cap and compacted into a 4.5 mm thick by 31 mm diameter pellet using a hydraulic press. X-ray intensity data were collected using a Panalytical® PW2400 sequential wavelength-dispersive XRF spectrometer with a chromium target X-ray tube. Element concentrations were calculated from the X-ray data using UniQuant® (version 5), a fundamental parameters quantitative analysis program. A specialized calibration based on catalyst reference materials and matrix-matched in-house standards was used to compensate for errors associated with the analysis of multi-phase materials. A customized background model with carefully selected fixed background points was used to improve accuracy and trace element analysis. A separate regression calibration curve based on pressed pellet specimens doped with 0 ppm, 10.0 ppm and 20.8 ppm Pt was used to detect ultra low-levels of Pt. Counting times of 600 seconds for the Pt peak ($L\beta_1$ X-ray line) and two background points were required to obtain a 2 ppm lower limit of detection.

X-ray diffraction (XRD) was carried out with a Scintag PADV 20/0 diffractometer (Cu K α Radiation) on material spread as a thin layer on an off-axis-cut "zero-background" quartz substrate. The Raman spectra were collected using with excitation of 488nm from an Innova 90Ar+ laser from Coherent.

EPMA MAPPING AND SEM ANALYSIS - For electron probe micro analysis (EPMA), selected pieces were mounted in epoxy. The mounted samples were ground and polished down to a final grit size of 1 μ m, and then carbon coated. Wavelength dispersive x-ray mapping was obtained in a JEOL 8200 electron probe analyzer. Semi-quantitative maps displayed in log wt% have the advantage of displaying elemental concentrations from trace (<1%), to minor (<10%), through to major (>10%) [6]. Conditions used for mapping were an accelerating voltage of 20keV, a beam current of 40nA, and a dwell of 100ms. ImageJ was used to process the maps and backgrounds [7]. Each background image was "blurred" using a maximum filter with a radius of 3 pixels before subtracting it from the elemental map. The subtracted maps were transformed from x-ray counts to log wt% using the relation $C_{\text{unknown}}/I_{\text{unknown}} = C_{\text{std}}/I_{\text{std}}$. C is the concentration in weight percent of the element in either the unknown or an analytical standard, I is the net x-ray intensity in counts/sec/ μ A for either the unknown or the standard. The resulting maps of the washcoat should be interpreted as powders suspended in epoxy.

For detection of extremely low levels of impurities on the surface of the washcoat, a small sample with several open channels was put on a stub with double stick tape and carbon coated. This eliminated any issues with contamination by previously polished samples. The sample was examined in a JEOL 6300F field emission gun Scanning Electron Microscope (SEM). Particles >~30-40nm were detectable using backscattered electron (BSE) imaging and energy dispersive x-ray spectroscopy (EDX).