

Effect of Accelerated Aging Rate on the Capture of Fuel-Borne Metal Impurities by Emissions Control Devices

Aaron Williams and Robert McCormick
National Renewable Energy Laboratory

Michael Lance, Chao Xie, and Todd Toops
Oak Ridge National Laboratory

Rasto Brezny
Manufacturers of Emission Controls Assoc

ABSTRACT

Small impurities in the fuel can have a significant impact on the emissions control system performance over the lifetime of the vehicle. Of particular interest in recent studies has been the impact of sodium, potassium, and calcium that can be introduced either through fuel constituents, such as biodiesel, or as lubricant additives. In a collaboration between the National Renewable Energy Laboratory and the Oak Ridge National Laboratory, a series of accelerated aging studies have been performed to understand the potential impact of these metals on the emissions control system. This paper explores the effect of the rate of accelerated aging on the capture of fuel-borne metal impurities in the emission control devices and the subsequent impact on performance. Aging was accelerated by doping the fuel with high levels of the metals of interest. Three separate evaluations were performed, each with a different rate of accelerated aging. The aged emissions control systems were evaluated through vehicle testing and then dissected for a more complete analysis of the devices. Results from these experiments show that increasing the rate of acceleration impacts the amount of fuel-borne metals that are captured by the catalyst, which subsequently impacts the catalyst performance. Beyond a certain threshold, the acceleration rate creates an artificial mechanism for catalyst deactivation. In the range of acceleration rates that were examined in this study, these effects were primarily isolated to the inlet of the catalyst whereas performance further down the length of the catalyst was mostly unaffected.

CITATION: Williams, A., McCormick, R., Lance, M., Xie, C. et al., "Effect of Accelerated Aging Rate on the Capture of Fuel-Borne Metal Impurities by Emissions Control Devices," *SAE Int. J. Fuels Lubr.* 7(2):2014, doi:10.4271/2014-01-1500.

INTRODUCTION

Metallic fuel contaminants such as sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) may be introduced into diesel fuel through a number of different sources. As one example, biodiesel production relies on sodium hydroxide or potassium hydroxide to catalyze the reaction of vegetable oils with methanol to form methyl esters. In this process, residual amounts of Na or K can be left behind. In addition, small amounts of Ca or Mg can be added to the fuel from the purification process [1,2]. These metal 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. Alkali metals are well known poisons for catalysts and have been shown to negatively impact the mechanical properties of ceramic

substrates [3,4]. 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.

The research described in this paper was motivated by previous work investigating the impact of these fuel-borne metal impurities on the full-useful-life durability of exhaust catalysts. In the previous study, an accelerated method was developed to expose catalysts to full-useful-life exposure levels of Na, K, and Ca coming from a biodiesel containing metals at the specification limit [5]. The ASTM International standard for biodiesel (ASTM D6751) currently limits 100% biodiesel (B100) to 5 parts per million (ppm) of Na+K and 5 ppm of Ca+Mg (effectively limiting B20 to 1 ppm Na+K and 1 ppm Ca+Mg). To accelerate exposure to these metals, a test fuel was doped with higher quantities of metal than normally allowable. The 150,000-

mile full-useful-life requirement of a Ford F250 pickup was simulated in 100 hours by doping a B20 with 14 ppm of K. This represented a 14x rate of acceleration for metal exposure. The results of this work raised questions about the impact of methods used for accelerated aging.

To investigate how the rate of accelerated aging impacts the catalyst, two additional experiments were run: 50 hours with B20 containing 28 ppm K and 200 hours with B20 containing 7 ppm K. In total this generated three systems aged at three different rates of acceleration; however, each system was exposed to the same total amount of fuel-borne K. The results of this research will help build upon the understanding of proper methods used for accelerated aging of exhaust emission control catalysts. This knowledge is not only important in guiding future studies to investigate the impact of biodiesel metal impurities, but may have broader application to studies looking at lubricant derived ash as well.

TEST METHODS

Catalyst Aging

The exhaust catalysts selected for accelerated aging studies were from a production 2011 Ford F250 pickup equipped with a 6.7L diesel engine. These systems included a diesel oxidation catalyst (DOC), selective catalyst reduction (SCR), and a diesel particulate filter (DPF). The DOC consisted of two separate monoliths mounted in series with a total volume of 4.35 L. The SCR system included a pair of copper/zeolite catalysts mounted in series with a total volume of 9.88 L. The DPF was a catalyzed SiC substrate and had a total volume of 8.2L. Further catalyst details are listed in Table 1. Three OEM exhaust systems were purchased from a local dealership to be used for accelerated aging. Each system was instrumented for temperature and pressure measurements and for exhaust sampling. These systems, as purchased from the dealership, were welded from end to end with no access to the individual catalyst components. Therefore, the DPF section was cut and flanged from the rest of the exhaust to allow for weighing the DPF to quantify ash loading. A schematic of the exhaust system is shown in Figure 1.

Table 1. Catalyst specification

Test Piece	D × L (in)	CPSI*	Coating
DOC #1	6.5 × 3.25	400	Pd rich
DOC #2	6.5 × 4.75	400	Pd rich
SCR #1	8 × 6	400	Cu-Cha**
SCR #2	8 × 6	400	Cu-Cha
cDPF	8 × 10	200	Pt:Pd

*cells per square inch
Cu-Cha = copper-chabazite

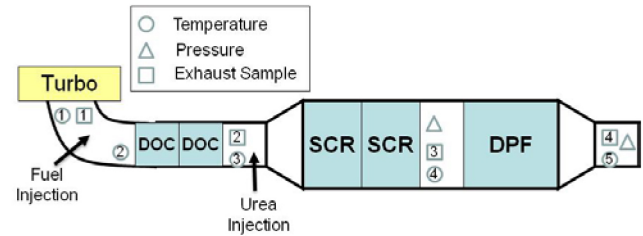


Figure 1. Schematic of exhaust system

For accelerated aging, these full exhaust systems were placed onto an accelerated aging platform, which was described in earlier studies [5,6]. The accelerated aging platform consisted of a Caterpillar 2008 C9 ACERT engine. This is an 8.8L, 300hp engine calibrated to meet the Tier III off-road emissions limit. The engine is turbocharged and direct injected and does not use an exhaust catalyst in its base configuration. By retrofitting the engine with exhaust emission controls, it served as a platform for exposing various catalysts and filters to exhaust gas from fuels containing metal impurities. The exhaust was retrofitted with a fuel injector placed 10 cm downstream of the turbo flange and 183 cm upstream of a diesel oxidation catalyst. This fuel injector was used to inject fuel that burned over the DOC, creating hot exhaust temperatures typical of a DPF regeneration event.

A three-mode test cycle was developed for the Caterpillar engine to achieve catalyst temperature and space velocity conditions consistent with operating parameters in an F250 pickup. The conditions for these three modes are shown in Table 2. This range of space velocities and temperatures was chosen based on data from the F250 pickup operating over the Federal Test Procedure (FTP) and US06 drive cycles on a chassis dynamometer. As the rate of accelerated aging was increased, the ratios of time among modes 1, 2, and 3 were adjusted. This was done to achieve the same amount of total time at the high-temperature condition experienced in mode 3.

Table 2. Catalyst aging conditions

Engine Mode	Time (min)	SCR SV (1/hr)	SCR inlet T (°C)
1 (low-temp operation)	15	20k	200
2 (high-temp operation)	15	57k	340
3 (regen operation)	30	57k	700

The B20 test fuels were made from a petroleum-based ultra-low sulfur diesel and a soy-based biodiesel, neither of which contained any measureable quantity of K at a detection limit of 1 ppm. Batches of B20 were blended in 250-gallon tote quantities and then doped with potassium dodecylbenzene sulfonate to achieve precisely controlled levels of K. Once the B20 batches were blended and doped, they were allowed to mix overnight.

with a paddle wheel agitator. A sample was then collected for analysis. Samples were collected from the top and bottom of the tote to ensure a homogeneous mixture of the dopant.

Fuel dopant levels were selected to simulate full-useful-life metal exposure coming from B20 at three different rates of accelerated aging: 7x, 14x, and 28x. As the K dopant level was increased, the duration of engine operation was reduced such that the total exposure to K would be identical in all three tests. These levels and durations of testing were chosen to achieve 150,000 miles worth of metal exposure, assuming normal vehicle operation with a B20 blended from B100 at the ASTM specification limit of 5 ppm K. This corresponds to a B20 fuel containing 1 ppm of the impurity. The three different aging scenarios are detailed in Table 3.

Table 3. Rates of accelerated aging

Rate of Accelerated Aging	K dopant level in B20 (ppm)	Duration of engine operation (hours)
7x	7	200
14x	14	100
28x	28	50

The catalysts were evaluated for signs of deactivation by installing the full exhaust system onto a Ford F250 pickup for emissions testing. This vehicle was certified to a Tier 2 Bin 8 emission limit of 0.2 g/mile NO_x . The vehicle was operated on a chassis dynamometer over the FTP cycle with emissions measurement following the U.S Environmental Protection Agency certification test methods. Prior to emissions testing, the catalysts went through a set of conditioning cycles to ensure that the catalysts were at the same state. This emissions testing was conducted with standard ultra-low sulfur diesel containing no measurable quantity of metals. Further details on procedures for emissions testing and catalyst pre-conditioning are described in Reference 5.

Catalyst Post-Mortem

At the completion of catalyst aging and vehicle emissions testing, the catalysts were cored and sectioned for detailed post mortem analysis. The exhaust system consisted of two DOC and two SCR monoliths mounted in series. Catalyst cores with approximately 1 inch diameter were taken down the length of each of these DOC and SCR bricks close to the radial center of each catalyst. Each catalyst core was then divided equally into four parts, as shown in Figures 2 and 3. From the inlet to outlet direction, the four parts were labeled as Inlet, Mid 1, Mid 2, and Outlet, respectively.

The harvested samples were analyzed for K content in the catalyst washcoat by scanning electron microscope-energy dispersive X-ray analysis (SEM-EDAX). Washcoat powders were scraped from each sample and ground into a fine powder for SEM-EDAX analysis. The washcoat powders thus obtained

were loaded onto carbon tapes, followed by carbon coating to minimize charging during elemental analysis. SEM-EDAX measurements were performed on a Hitachi S4800 FEG-SEM with an EDAX Genesis SDD-EDS detector. The operation voltage and current were 25 kV and 20 μA , respectively. Elemental analyses were done at 2,000x magnification, corresponding to a sampled area of 48 μm by 64 μm . For all samples, the elemental analyses were repeated three times through randomly measuring three different locations, and the results were averaged. The elemental weight percent was calculated using the fundamental parameters method without any standards, and the contribution from cordierite debris was subtracted from the final result.

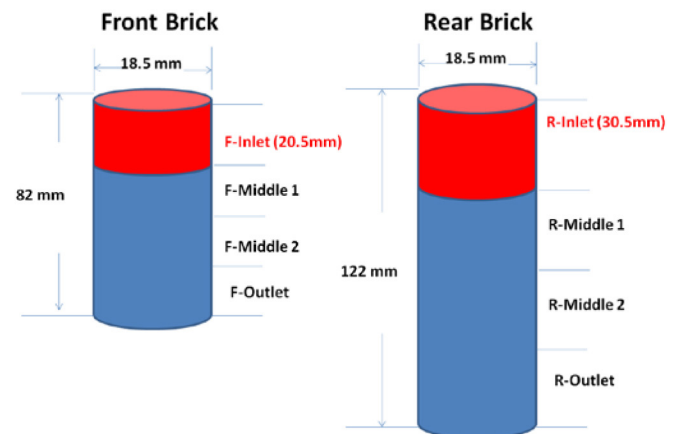


Figure 2. DOC Cores

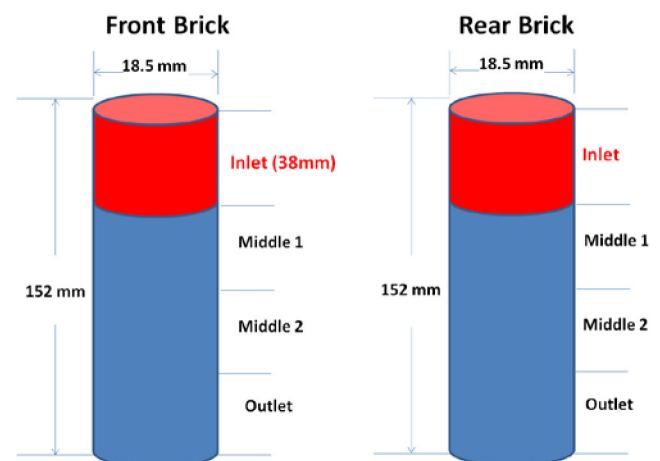


Figure 3. SCR Cores

Measurement of the carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NO) oxidation activity of the DOC samples and the NO conversion of the SCR samples was conducted in a bench flow reactor. Conditions used in the bench flow reactor experiments are shown in Tables 4 and 5. The temperature of the catalyst sample was ramped from 100°C to 650°C at a rate of 10°C/min.