

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

2011-01-1136

Published
04/12/2011

Aaron Williams, Robert McCormick and Jon Luecke
National Renewable Energy Laboratory

Rasto Brezny
Manufacturers of Emission Controls Assoc.

Andreas Geisselmann
Umicore AG & Co KG

Kenneth Voss and Kevin Hallstrom
BASF Corp.

Matthew Leustek, Jared Parsons and Hind Abi-Akar
Caterpillar Inc.

doi:[10.4271/2011-01-1136](https://doi.org/10.4271/2011-01-1136)

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

**Documents**

Document Sharing Hub

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 Cuzeolite 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 NOx 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 high 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

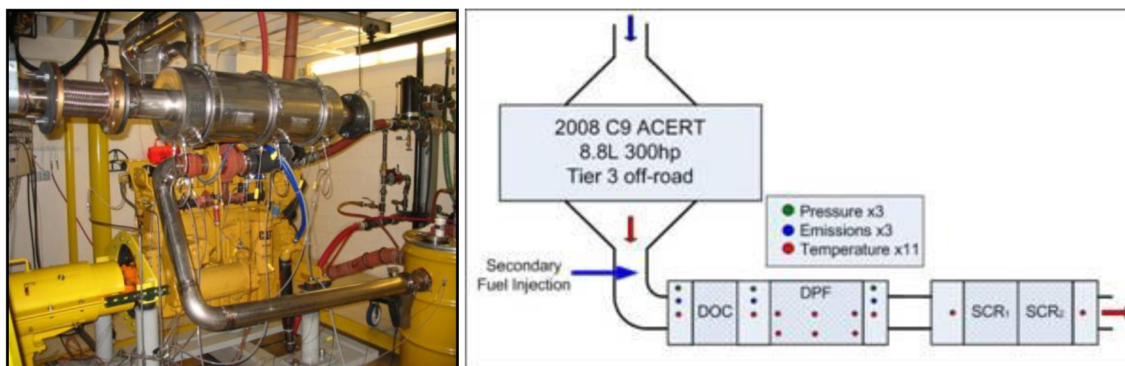


Figure 1. Experimental setup

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

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.

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.

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

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	--	--

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 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.