

# Analysis of Ash in Low Mileage, Rapid Aged, and High Mileage Gasoline Exhaust Particle Filters

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## ABSTRACT

To meet future particle mass and particle number standards, gasoline vehicles may require particle control, either by way of an exhaust gas filter and/or engine modifications. Soot levels for gasoline engines are much lower than diesel engines; however, non-combustible material (ash) will be collected that can potentially cause increased backpressure, reduced power, and lower fuel economy. The purpose of this work was to examine the ash loading of gasoline particle filters (GPFs) during rapid aging cycles and at real time low mileages, and compare the filter performances to both fresh and very high mileage filters. Current rapid aging cycles for gasoline exhaust systems are designed to degrade the three-way catalyst washcoat both hydrothermally and chemically to represent full useful life catalysts. The ash generated during rapid aging was low in quantity although similar in quality to real time ash. Filters were also examined after a low mileage break-in of approximately 3000 km. It was found that ash levels as low as 1 g can have a significant impact on filtration efficiency with a relatively small impact on backpressure. The location, composition, and morphology of low ash loadings was compared to a filter aged to 150,000 real miles.

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## INTRODUCTION

Direct injected gasoline (GDI) engines can create significant amounts of soot under certain operating conditions such as cold start and high load. California LEVIII and U.S. Tier 3 require a tailpipe particulate matter (PM) maximum of 3 mg/mi, with 2017-2021 model year phase-in. In Europe, Stage 6 particle number (PN) standards for DI vehicles become 90% lower at  $6 \times 10^{11}$  particles/km in September 2017. New tests like real world driving emissions (RDE) will cover more driving conditions than older tests. Wall flow ceramic filters are one well known way to remove exhaust PM and PN. The filter may be used with or without a catalytic washcoat and is typically located downstream of a conventional three-way catalyst. In relatively clean conditions compared to diesel particle filters (DPFs), GPFs can usually offer filtration efficiencies on the order of 70-80% [1]. This is due to the much lower soot output of GDI engines compared to diesel engines. GDI soot emissions primarily occur during cold start [2].

There has been a great deal of research and development pertaining to ash deposition, origination and the operating conditions under which ash is created on diesel engines [3], but not as much literature is available on gasoline engine ash studies. In one previous gasoline filter study, it was found that about 60 g of non-combustible material (ash) was retained in filters installed on two different turbocharged GDI vehicles over 130,000 and 150,000

mi on US EPA Standard Road Cycle (SRC) [4]. About 2/3 of the ash was located on the filter walls, with the remainder in the plug region. Half of the ash mass was derived from lubricant additives, and the other half consisted mainly of mainly iron oxide from corrosion of steel exhaust manifold/piping and catalytic washcoat from erosion of upstream three-way catalysts (TWCs). While the backpressure of the exhaust system doubled at high vehicle speed (80 mph), the impact on fuel economy was not measurable. The present study aims to understand ash accumulation in GPFs at very low mileages and on accelerated aging cycles that have short time durations, and compare the ash quality and quantity to a full useful life (FUL = 150,000 mi) GPF. It is of interest not only to explore if accelerated aging cycles can accurately capture ash accumulation characteristics, but also what changes in GPF performance occur at low ash quantities.

## EXPERIMENTAL

### GPF Sample Designations and Nomenclature

Several GPF samples were analyzed in this study, both green and aged, and the sample designations are in Table 1. The filter substrates were cordierite wall-flow monoliths with at least 1.0 g/in<sup>3</sup> and no more than 2.0 g/in<sup>3</sup> of three-way washcoat containing Pd and Rh. The total porosity of the filters before washcoating was approximately

65% with a mean pore size of approximately 20-22  $\mu\text{m}$ . Filter dimensions generally were a diameter of 5.66", a length of 4", cell density of 300 cells per in<sup>2</sup>, and 305  $\mu\text{m}$  (12 mil) walls.

Table 1. GPF samples analyzed in this study.

| Sample designation | GPF status                     | Total filter vol (L) |
|--------------------|--------------------------------|----------------------|
| FUL                | EPA SRC (150K mi)              | 2.5                  |
| FM50h              | Four mode 50 h dyno            | 1.6                  |
| FM60h              | Four mode 60 h dyno            | 1.6                  |
| B3.2               | Burner aged (3.2g/L ash)       | 1.7                  |
| 3k1, 3k2           | 3000 km on road (random drive) | 1.6                  |
| A1                 | Artificial ash (high)          | Not applicable       |
| A2                 | Artificial ash (mid)           | Not applicable       |
| A3                 | Artificial ash (low)           | Not applicable       |
| Green              | Fresh (zero ash)               | 1.6                  |

Table 2. Four-mode aging cycle details.

| Aging cycle designation | Peak temperature | Fuel dopant(s)     |
|-------------------------|------------------|--------------------|
| Four mode 50h           | 1040°C           | ZDDP, Ca sulfonate |
| Four mode 60h           | 940°C            | Organophosphate    |

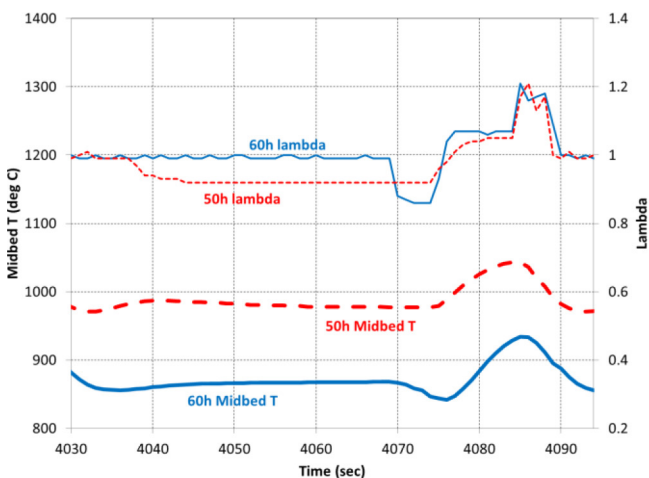


Figure 1. Midbed temperatures and air/fuel ratio (lambda) measured during two types of four mode aging cycles on an engine dynamometer with TWC+GPF systems. The 50h cycle traces are shown in red and the 60h cycle traces are shown in blue. An example of one cycle is shown; the cycle is repeated for the specified number of hours.

The sample called "FUL" is from the previous high mileage study [4] and was aged to 150,000 mi on EPA SRC in a TWC+ GPF system. This filter was significantly larger than the other filters in Table 1. FM50h and FM60h were two filters aged on an engine dynamometer using two different four mode aging cycles to simulate stoichiometric, rich, and lean conditions experienced in the exhaust of a gasoline vehicle, but at accelerated aging temperatures. The traces of midbed (pre-GPF temperature and air/fuel ratio (lambda) are in Figure 1. Each four mode cycle was about one minute in duration and repeated for the specified number of hours. A TWC was installed upstream of each GPF. The fuel was doped with contaminants to simulate high mileage poisoning of three-way catalysts. The details of each four mode cycle are in Table 2, along with key differences in peak temperatures and

fuel dopants, including ZDDP (Zinc dithiodialkylphosphate), calcium sulfonate, and an organophosphate. These dopants were not intended to match on-road GPF ash accumulation.

An accelerated aging burner system described in [5] was used to load catalyzed 1.73L filters with ash to levels between 3.2 and 20g/L in order to investigate the effects of ash on both filter pressure drop and catalytic performance [6]. The sample with the lowest loading, 3.2g/L ash, is discussed in this article and is labeled B3.2.

The filters designated 3k1 and 3k2 in Table 1 were each aged to 3000 km on the road. Filters were installed on a 2.3L GTDI vehicle downstream of a TWC. There was no set cycle; most of the mileage was at higher speeds on interstate highways in southeastern Michigan. The engine was at low but non-zero mileage. The engine oil was 5W-30 synthetic blend that met GF-5 specifications.

Artificial ash-containing GPF samples were created by taking core samples from a fresh, washcoated GPF and doping them with various amounts of artificial ash. The samples were designated A1, A2, and A3. A fresh (Green) filter was used to compare to the ash-containing samples. Sample location nomenclature used in this study is described in Figure 2. In a wall flow filter, the gas enters the channels that are not plugged and crosses the porous wall; therefore, the wall has an inlet side and an outlet side. The front of the filter is the first section exposed to the exhaust gas, followed by middle and back.

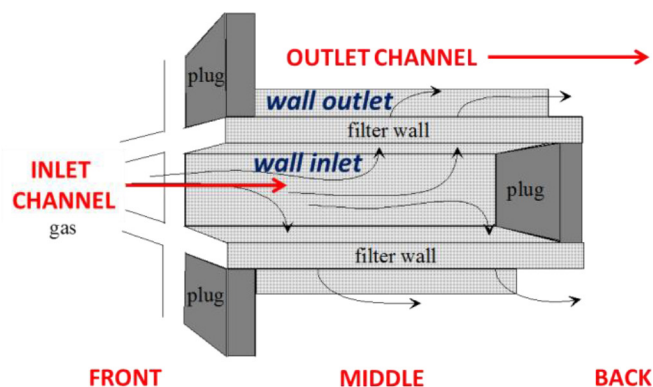


Figure 2. Nomenclature used for sample locations within a GPF.

## Engine Testing

Backpressure and filtration efficiency of full-size GPFs were measured using a 2.0 L turbocharged GDI (GTDI) engine in a dynamometer cell at the Ford Research and Innovation Center equipped with two Dekati Mass Monitors that measured particle mass. Two engine speed/load/lambda points were selected: 1) a rich, low speed, moderate temperature point to check for clean filtration efficiency, and 2) a lean, high speed, high temperature point to check clean backpressure. Hot, lean conditions were used to oxidize soot in the GPF before the filtration efficiency was checked.

## Analytical Methods

GPFs were scanned on a computed tomography (CT) scanning tool at the Non-Destructive Evaluation Laboratory, Ford Research and Innovation Company. Filter samples were also scanned via X-ray microCT at the

Harvard Center for Nanoscale Systems to produce three dimensional representations of the ash accumulation within the filters. Three dimensional data were collected with an X-tek HMXST 225 microCT X-ray CT instrument, which was discussed in detail in [7] and is capable of approximately 1.2 $\mu$ m voxel size. CT data post processing was done via VG StudioMax 3.0.

Full size filters were tested at room temperature at Ford's Powertrain Fuel Systems Lab (PFSL) to provide backpressure data for filter wall permeability estimations. Permeability was also derived from the backpressure measured on a cold flow bench with filter cores (1" in diameter) cut from the bricks. Full length one inch diameter cores were extracted from the substrate. Pressure drop across each core was measured at room temperature over a range of flow rates so that estimations could be made for wall and ash permeability.

A mercury intrusion porosimeter (MIP) from Micromeritics was used to confirm microstructural filter properties such as porosity and pore size distribution. Macrostructural filter properties such as wall thickness and cell density were confirmed by optical microscopy, and careful filter weights were taken of various sections to confirm washcoat loadings and washcoat distribution.

Core samples from aged GPFs (FUL, FM50h, FM60h, 3k1, 3k2) were analyzed using X-ray fluorescence (XRF) at Ford to determine their elemental composition. The cores were taken from the front, middle, and back portions of each filter, or sometimes only the front and back, and end plugs were removed. The specimens were prepared by first grinding them into a fine, homogeneous powder using a carbide grinding dish. A 5 g sample of each powder was then mixed with 0.5 grams of Chemplex X-Ray Mix and compacted into a pellet using a hydraulic press. The pellet was analyzed using a PANalytical PW2400 XRF Spectrometer and UniQuant5 quantitative analysis program (4/14/05 calibration). A fresh filter analysis done previously was used as background.

Artificial ash samples A1, A2, and A3, were created by taking three core samples from a fresh, catalyzed GPF (end plugs removed) and grinding them into a fine powder using a Retsch RM200 Mortar Grinder with carbide mortar and pestle. Portions of the ground catalyzed GPF powder were blended with various amounts of artificial ash composed of Fe<sub>2</sub>O<sub>3</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, CaSO<sub>4</sub>, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and NiO to simulate high ash (A1), mid ash (A2), and low ash (A3) loaded filters. Samples of 5 g of each powder were pelletized and analyzed as described above for the other GPFs.

Scanning electron microscopy (SEM) was used at Ford to determine the ash particle morphology on the inlet wall surface of various filters. Electron probe microanalysis (EPMA) was also performed at Ford to determine ash composition and location. Selected pieces of cores were vacuum impregnated in Epofix epoxy. The mounted samples were ground and polished down to a final grit size of 1  $\mu$ m, and then carbon coated. Wavelength dispersive X-ray mapping was obtained in a JEOL 8200 EPMA. Semi-quantitative maps displayed in log wt% have the advantage of displaying elemental concentrations from trace (<1%), to minor (<10%), through to major (>10%) as proposed by Newbury and Bright [8]. Conditions used for mapping were an accelerating voltage of 15keV, a beam current of 30 nA, and total dwell time of 300 ms

from multiple accumulations. ImageJ [9] was used to process the maps and one background image for each map. 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/ $\mu$ A for either the unknown or the standard.

GPF post mortem analysis were done at MIT on several relative size scales since relevant ash-substrate interactions occur over a wide size range, from sub- $\mu$ m to tens of cm. General imaging and elemental analysis were performed by an FEI/Philips XL30 Field Emission Gun (FEG) Environmental Scanning Electron Microscope (ESEM) with an EDAX Energy Dispersive X-ray Spectroscopy (EDX) detector. ESEM does not require extensive sample preparation, such as C/Au-coating, and detailed use of this instrument was discussed in [10].

The filters were carefully cut into small, less than 1 cm<sup>3</sup>, sections from the filter middle and back sections for destructive analysis and imaging. Cross sections of the GPF samples were prepared on the  $\mu$ m-mm scale by a JEOL Cross Section Polisher (CSIM) which uses argon ion milling, as discussed in [11]. The ESEM was used for imaging of both inlet filter wall surfaces and wall cross sections prepared by the CSIM. Cross sections prepared by CSIM enable the direct observation of ash penetration into the filter wall and into the filter surface pores.

## RESULTS AND DISCUSSION

### Filtration Efficiency and Backpressure

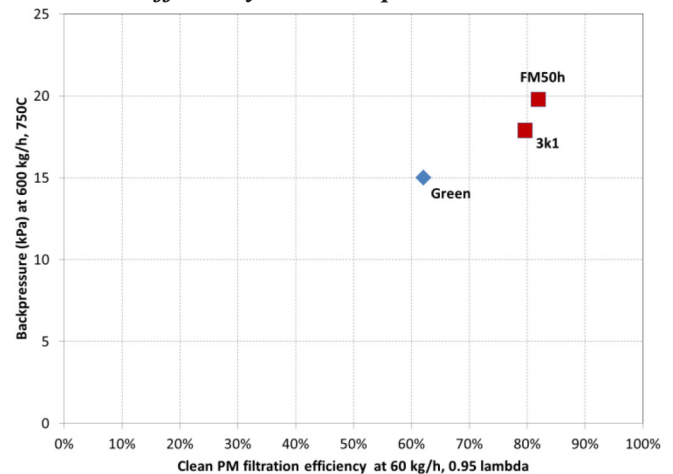


Figure 3. Clean backpressure and mass filtration efficiencies of Green, 3k1, and FM50h washcoated GPFs measured on a 2L GTDI engine.

The FM50h and 3k1 samples were available for a performance comparison on the engine dynamometer to a green filter of similar composition. The clean backpressure was measured at exhaust conditions of about 600 kg/h and 750°C, while the initial mass filtration efficiency was measured at a rich air/fuel ratio and an exhaust flow rate of only 60 kg/h (Figure 3). A significant improvement in initial filtration efficiency from about 60% green to 80% at 3k km or after 50h dyno aging was noted. The backpressures of the aged samples were about 3 to 5 kPa higher