Biofuels Impact on DPF Durability

Michael J. Lance, Todd J. Toops, Andrew A. Wereszczak, John M.E. Storey, Dane F. Wilson, Bruce G. Bunting, Samuel A. Lewis Sr., and Andrea Strzelec

Oak Ridge National Laboratory

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PM040

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Overview

Timeline

- Start: October 2009
- End: September 2012
- 50% complete

Budget

- Total Project Funding
  - DOE-$1.05 M
- Funding Received:
  - FY10: $350K
  - FY11: $350K

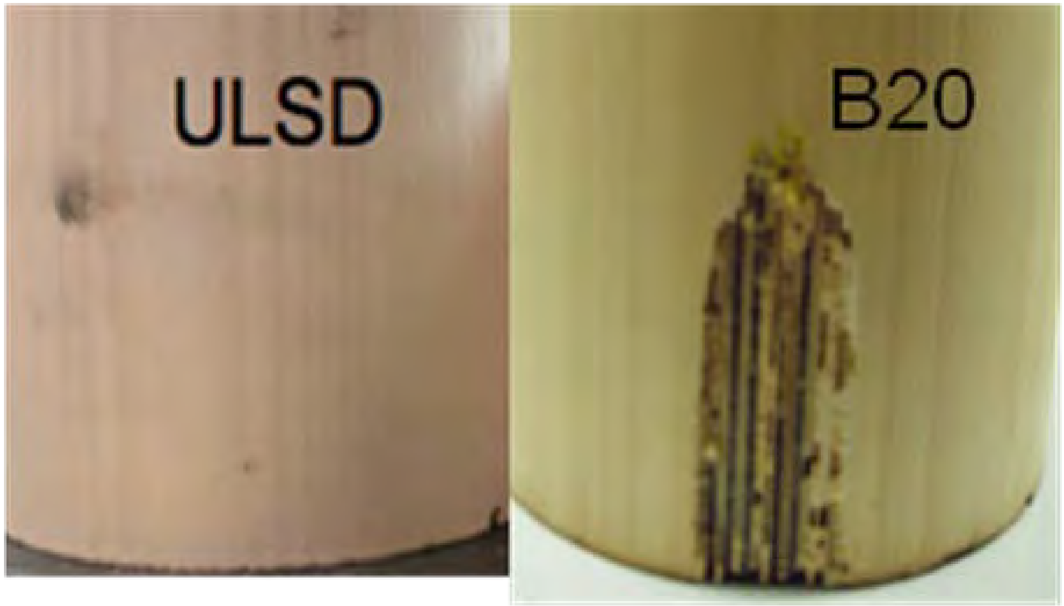
Barrier

- [There is] inadequate data on the effects of fuel properties (other than sulfur) on exhaust emission control systems, and widely-accepted test procedures to measure these effects do not exist. Furthermore, suitable test equipment and universally-recognized test procedures to generate this knowledge base are not available.
- The knowledge base is inadequate for determining the effect of fuel properties on the deterioration rates and durability of engine fuel system and emission control system devices and components.

Partners

- General Motors

Background: Possible Impact of Biofuel Blends on Cordierite PM Filters was Observed



B20 filter showed significant damage (filter removed from can 3 months after use)

- Uncatalyzed cordierite DPFs were used to collect PM for studies of biodiesel effects on PM properties.
- Four biodiesel blends (B0 (ULSD), B5, B20 and B100 using Soy Gold®) were run on a Mercedes 1.7L engine.
- What appeared to be corrosive attack of the cordierite increased with biodiesel content under low load (1500 rpm, 2.6 bar) conditions.
- Area of damage is region where water would be likely to condense and be held in the matting.

Project Objective

To characterize changes in the microstructure and material properties of diesel particulate filters (DPFs) in exhaust gas produced by biodiesel blends.

Milestones

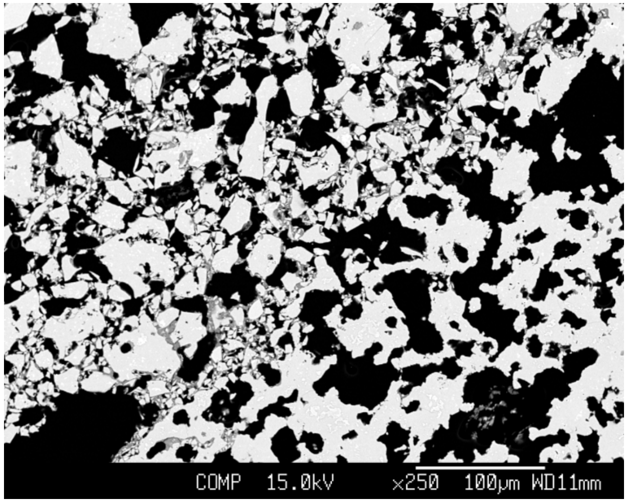
- FY10
  - Replicated initial engine test that produced DPF degradation.
  - Collected solid and semi-volatile particle emissions using ULSD and biodiesel blends and measured their chemical composition using GC-MS.
  - Developed finite element stress model, using μ-FEA©, to relate experimental compressive loading of the o-ring test geometry to associated failure stress.
- FY11
  - Jan-11 Milestone: Conducted accelerated chemical attack of SiC and cordierite filter materials with acids found in biodiesel exhaust condensate.
  - Feb-11 Milestone: Developed testing methodology for measuring DPF filter degradation using changes in substrate mechanical properties (elastic modulus and fracture strength).

Approach

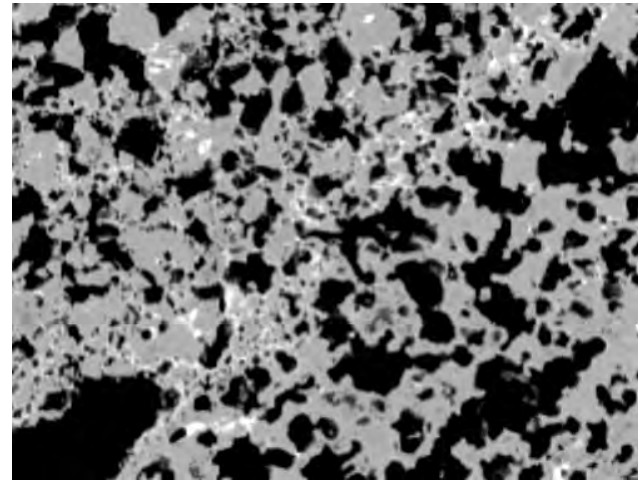
- Characterize the residue collected from the original experiment that produced cordierite corrosion with biodiesel operation.
- Attempt to repeat the experiment to attempt to reproduce the degradation.
- Measure the chemical composition and pH of exhaust condensate and PM generated by a diesel engine running with ULSD and biofuel blends under different loads using two different engines.
- Corrode the filter materials using acidic species found in biodiesel exhaust.
- Develop a mechanical strength test to separately probe degradation in the skin and the interior of the DPF.

Microstructural Comparison of DPF Outer Skin to DPF Interior

Scanning Electron Microprobe

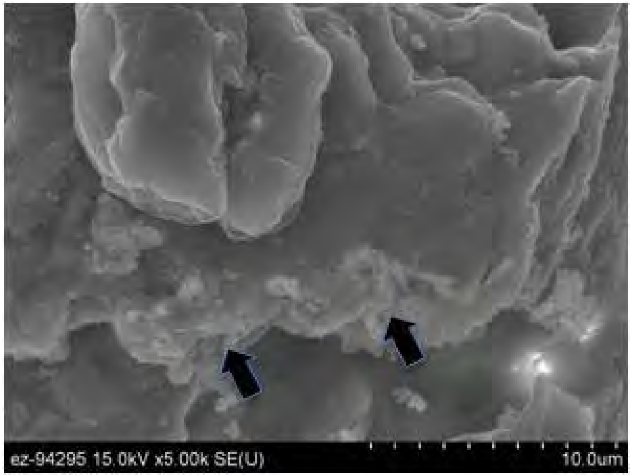


EPMA map of Silicon



- Since the degradation of the DPF bricks appeared to be localized in the skin and not the interior, electron probe microanalysis (EPMA) was used to compare the two regions.
- The skin of the DPF is different than the interior channels:
  - The interior (channels) appear more porous than the skin which is required for the filter to allow gas to permeate through the walls of the channels but not out of the brick into the padding.
  - The skin also has a broader particle size distribution than the interior presumably to increase its packing density.
  - The skin appears to have at least two phases present; a dense cordierite phase and a glassy grain boundary phase. A fiber phase was also observed in the skin.
  - The glassy grain boundary phase appears to be rich in Si and low in Mg and Al compared to the cordierite grains.

Microanalysis on Debris collected from B100 filter

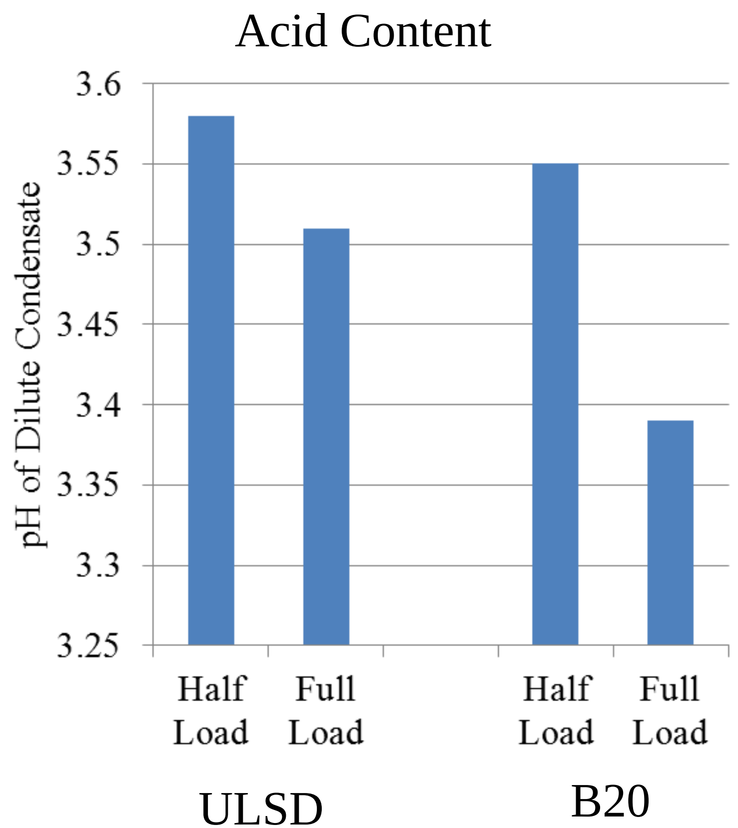


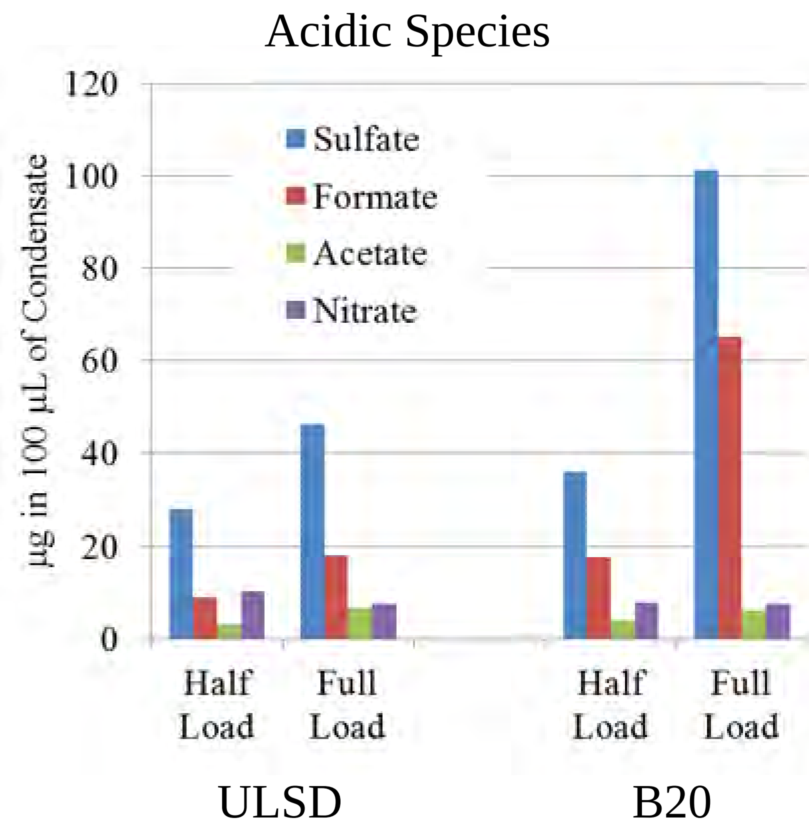
- EDS spectra were collected from the edge of cordierite particles since this is where corrosion products would be located.
- The arrows indicate regions where high amounts of Cl, Na, K, Ca, and S were detected. Fe, Cr and Cu were also seen in some regions.
- These elements were not observed in significant amounts in either the skin or the interior channels of the as-received DPF.
- Since many of these element can be found in both the lube oil and the tumescent padding, no compounds that would indicate corrosion of cordierite were conclusively found.

Attempt to Reproduce Filter Degradation

- Four DPFs were loaded with soot using the same Mercedes engine that produced initial DPF degradation. Engine was operated at 1500 rpm and 2.6 bar.
- Initial degradation occurred with Soy Gold but this test used SME fuel from Renewable Energy Group (REG) which was certified by Southwest Research Institute (SWRI) and GC-MS at Oak Ridge.
- The surface of the DPF after being exposed to certified B100 exhaust and storage for 3 months showed no degradation.

Acidic Content and Species in Condensate

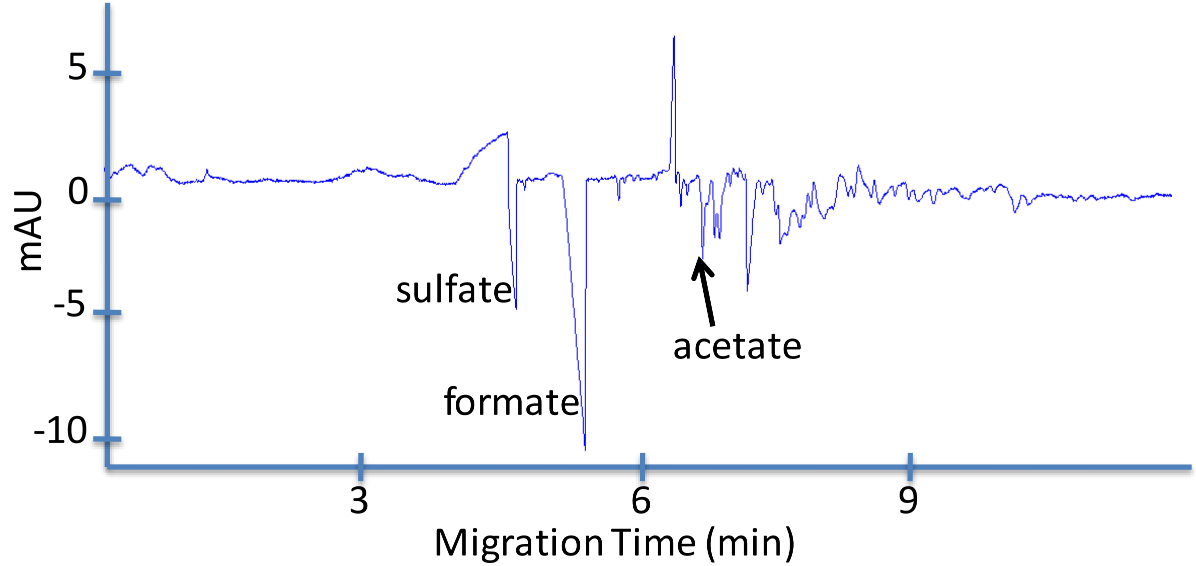




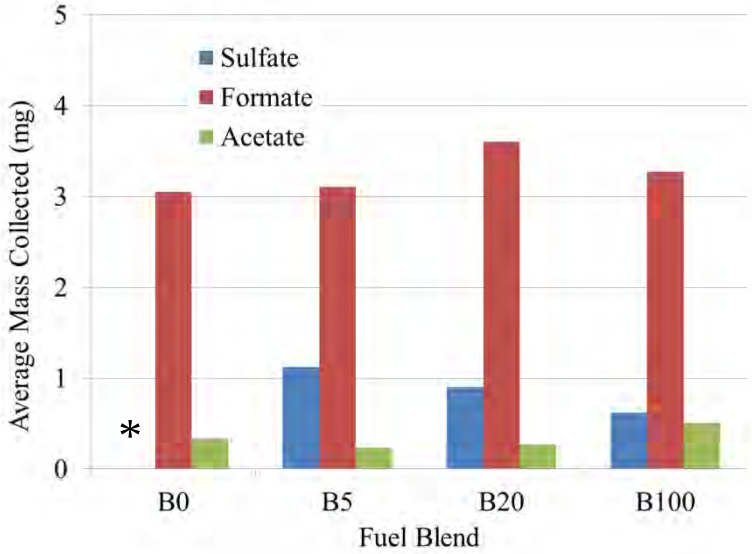
- Condensates were collected from the exhaust of ULSD (B0) and B20 fuels run on an air-cooled light-duty, single-cylinder (high NO_x & PM) Hatz engine at half and full loads.

- B20 combustion results in a significant increase in sulfuric and formic acid and total moles of H^+ in the exhaust gas, particularly under full-load conditions.

Capillary Electrophoresis identified key inorganic and organic acids



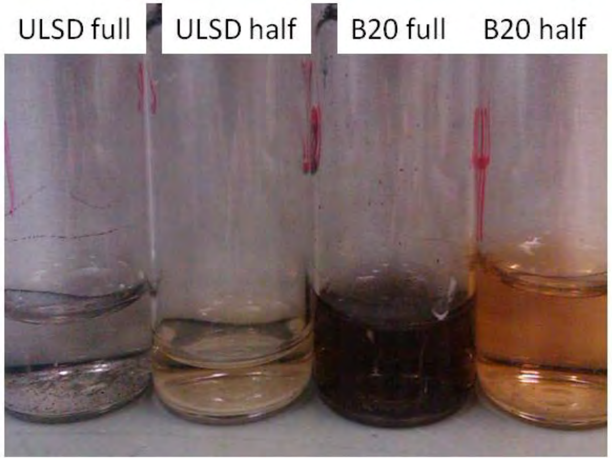
- Raw exhaust condensate collected in impingers.
- Mercedes 1.7 L turbo diesel, 1500 RPM, 2.6 BMEP load, B0, B5, B20, and B100 fuels. Low NO_x and no aftertreatment.
- Condensate composition used to formulate solutions for corrosion exposure.



*Note: sulfate present, but not quantifiable for B0

Analysis of Biodiesel PM Showed Hydrophilic Behavior

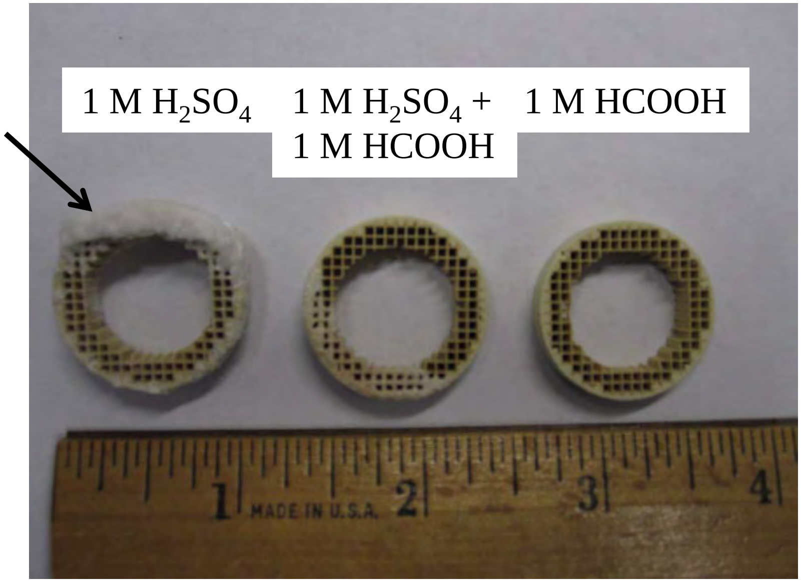
<u>Water extract from the PM collected from Hatz engine test</u>

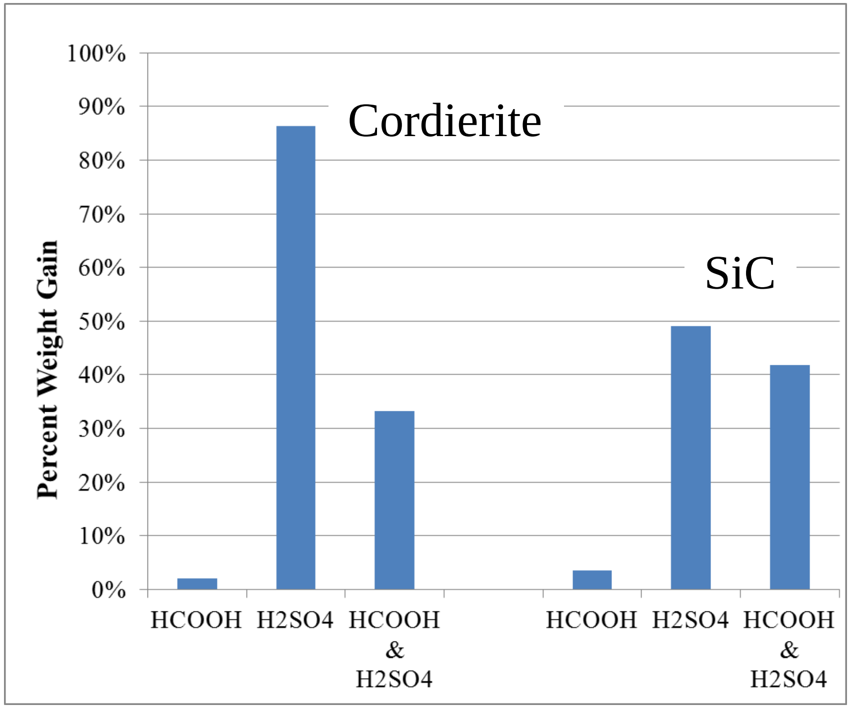


- The B20 full-load PM appears to be more soluble in water (hence the darker appearance of the extract above).
- GC-MS showed more polar species present in the B20 soot than the ULSD, which would explain its hydrophilic behavior.
- Biodiesel PM is able to retain water better than the ULSD PM thereby allowing aqueous corrosion to occur in the filter.

Accelerated Chemical Attack of Ceramic DPF Materials

Cordierite

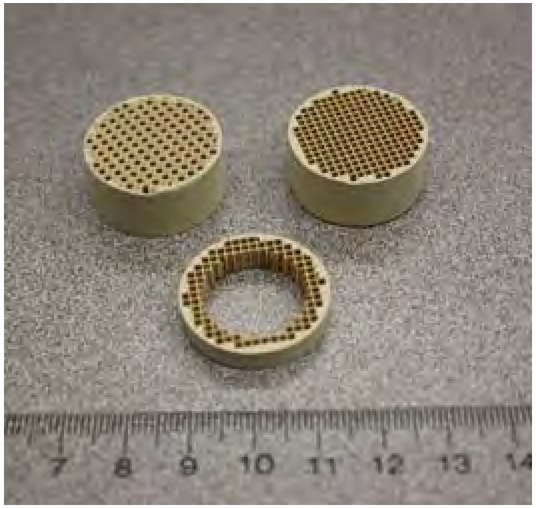




- DPF samples were dip tested in 1 M solutions of both sulfuric and formic acid and a 50:50 mixture of the two for 2 months followed by 1 month of drying in air.
- Upon drying, the cordierite formed Al and Mg sulfates (see arrow above). No pure formic acid attack was observed.
- The skin of the SiC sample contains alumino-silicate fibers that are susceptible to corrosion from sulfuric acid.
- The most likely mechanism is due to the condensate evaporating slowly, resulting in long exposure to a very concentrated acidic solution.

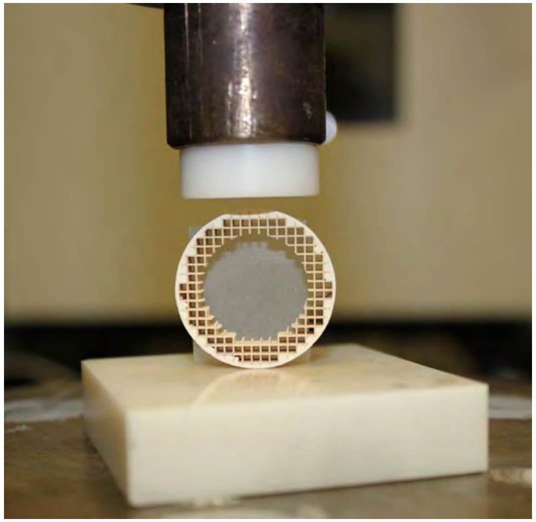
Standardized Methodology for Measuring DPF Degradation

Cordierite test specimen



SiC test specimen

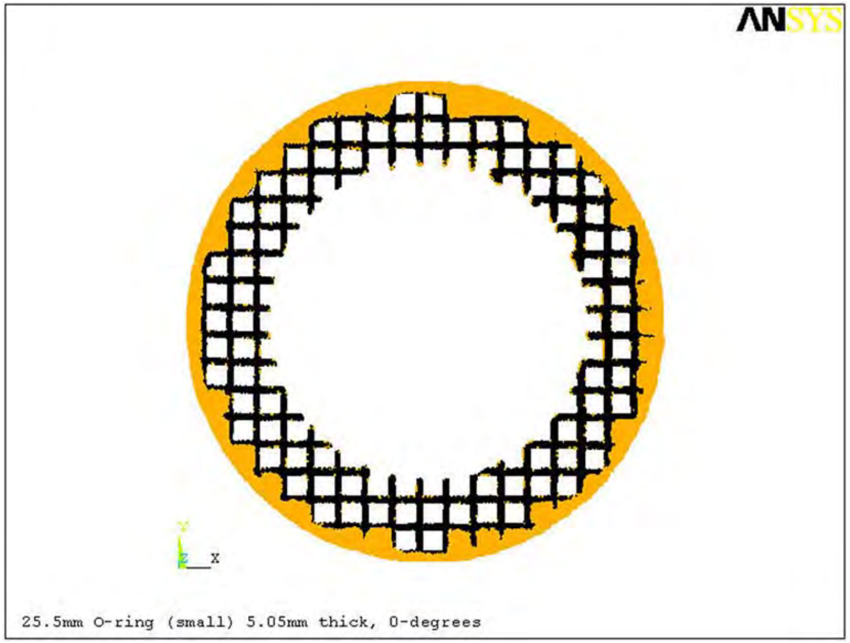
O-ring Test



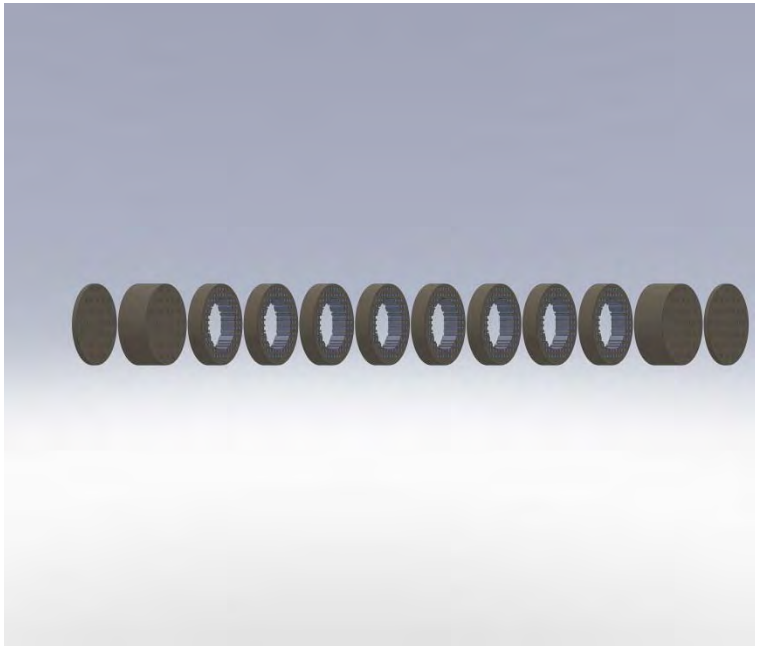
- Substrate fracture strength and elastic modulus are sensitive to DPF degradation modes such as micro-cracking and grain boundary attack that are difficult to observe with chemical or microscopic techniques.
- Our approach uses widely-available 1” by 3” DPF cores that can be run in an engine test and later sectioned and tested to determine if the DPF material has degraded.
- O-ring and ring-on-ring biaxial flexure test geometries separately test the outer skin and the interior channels, respectively.

DPF Durability Test

Recreated DPF Architecture



Multiple Samples Harvested from one DPF



- A digital picture of the o-ring was taken, preprocessed through micro-FEA software, and inputted into ANSYS.
- The µ-FEA technique allows one to estimate the moment of inertia of the complex DPF architecture and thus measure the material properties directly.
- A single DPF core will provide multiple samples which are necessary to improve the statistical significance for the strength and modulus measurements.

Collaborations

- This project partners with General Motors through project P18519-20091 since both have an interest in characterizing DPF substrate mechanical properties.
- We have been in communication with NGK concerning corrosion of DPF materials and they have provided samples for further analysis.

Future Work

- Baseline measurement of elastic modulus and fracture strength of SiC and cordierite 1 by 3" DPF cores will be conducted in order to establish a testing methodology for measuring DPF degradation during operation.
- Using this method, accelerated aging with Na and K doping in order to simulate long-term biodiesel exposure will be conducted and DPF material degradation will be measured.
- The effect of regeneration and subsequent ash build-up on the DPF substrate materials will also be measured in order to determine if biodiesel ash (known to be high in Na and K) acts as a fluxing agent with the substrate.
- Measure the effect of thermal cycling from regeneration on the DPF mechanical properties.

Summary

- Biodiesel operation (especially at full load) showed an increase in acid content and sulfuric and formic acid in the exhaust condensate under some conditions.
- The largest chemical difference between the biodiesel and ULSD soot was the increased hydrophilicity of biodiesel soot. This may explain the corrosion of the B100 sample as the soot could retain water adjacent to the filter better than the ULSD soot.
- DPF materials showed significant corrosion in 1M H_2SO_4 but only while the sample dried. Drying increases the local concentration of the acid allowing for the formation of Al and Mg sulfates. A similar mechanism may have produced the corrosion observed with biodiesel operation.
- The mechanical testing of a simple o-ring specimen geometry harvested from 1” by 3” DPF cores has potential to be an effective means to quantify degradation in DPFs.