Biofuels Impact on DPF Durability

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PM040

Overview

Timeline

- Start: October 2009
- End: September 2013
- 64% complete

Budget

- Total Project Funding
  - DOE-$1.35 M
- Funding Received:
  - FY10: $350K
  - FY11: $350K
  - FY12: $300K

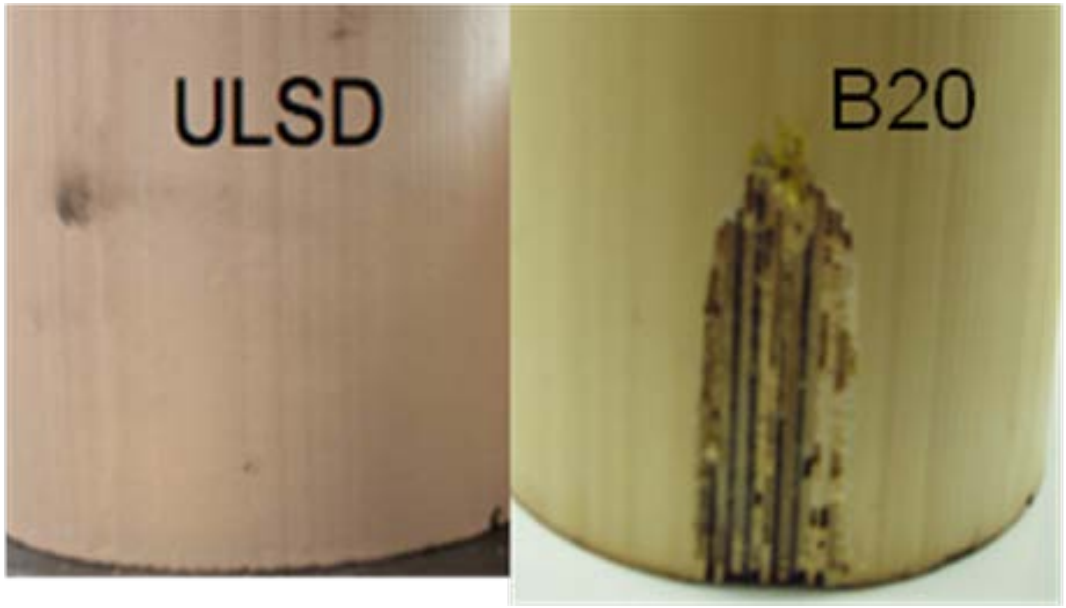
Barrier

- Page 2.4-3: [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.
- Page 2.4-3: 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

- Ford Motor Company, National Renewable Energy Laboratory (NREL), Manufacturers of Emission Controls Association (MECA), National Biodiesel Board (NBB), Corning.

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. Attack occurred mostly at the outer skin.

Project Objective

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

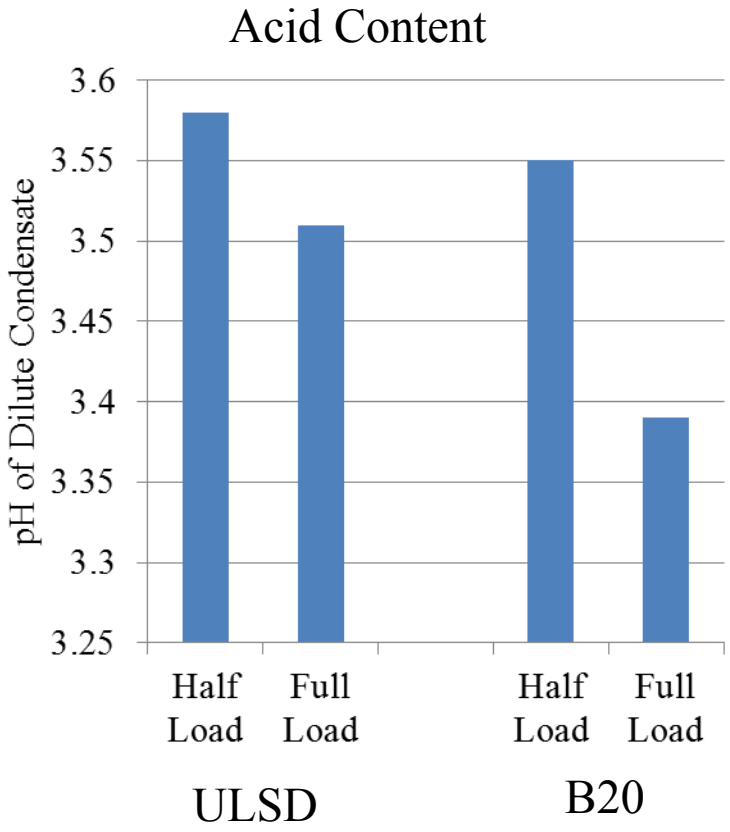
Milestones

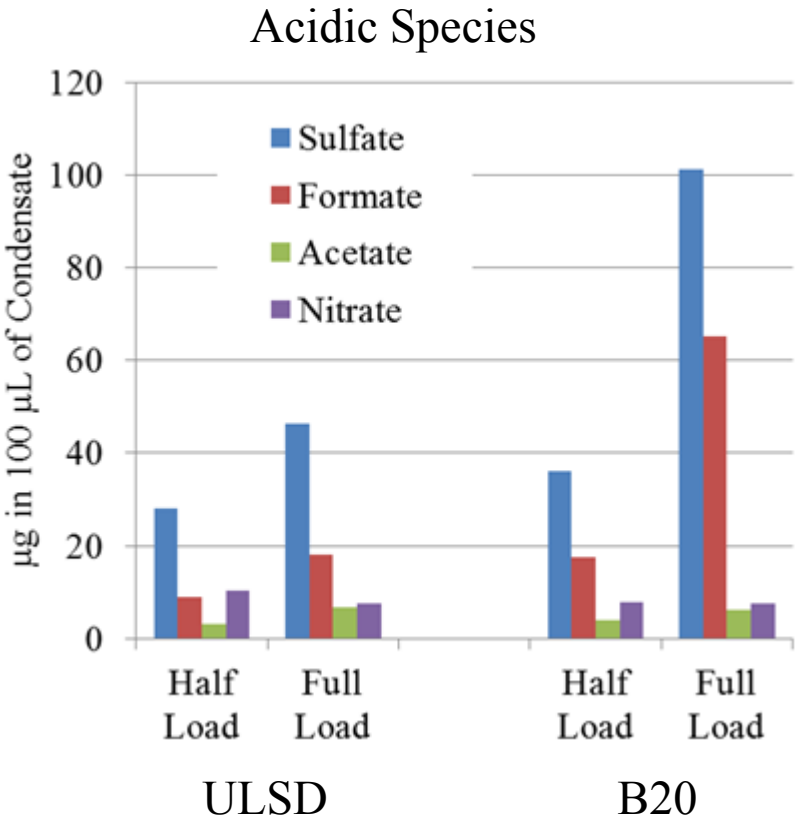
- FY10 & 11
  - Replicated initial engine test that produced DPF degradation.
  - Collected solid and semi-volatile particle emissions using ULSD and biodiesel blends using two different engines and measured their chemical composition with GC-MS.
  - Conducted accelerated chemical attack of SiC and cordierite filter materials with acids found in biodiesel exhaust condensate.
  - Measured elastic and fracture properties of SiC and cordierite materials using FEA-based flexure testing.
- FY12
  - Jan 12 Milestone: Installed engine-generator (or gen-set) for unattended long-term accelerated testing of DPFs with biodiesel and other fuels.
  - Mar 12 Milestone: Identified superiority of DPF mechanical properties testing in pure tension.
  - Mar 12 Milestone: Received and commenced analysis of NREL/Ford/MECA collaboration aging samples.

Approach

- Low-Temperature Corrosion
  - 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.
  - Repeat the experiment in order to reproduce the original degradation.
- Thermal Aging and Ash Accumulation
  - Develop a mechanical strength test to measure DPF degradation following exposure to biodiesel.
  - Collaborate with NREL biodiesel team to characterize light-duty ash accumulation from B20 metal impurities.
  - Establish operation of 24/7 gen-set for low-cost, flexible, accelerated aging of DPFs with diesel and biodiesel exhaust.

Acidic Content and Species in Condensate were Measured





- 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.

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. 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.
- Likely failure mode was reduction in binder tensile strength in the DPF skin due to biodiesel exposure. Original bricks were uncatalyzed and the skin had yet to be completely sintered.

Thermal Aging and Ash Accumulation

Biodiesel contains elevated metal levels

Property	ASTM Method	Limits
Ca + Mg	EN 14538	5 ppm
Na + K	EN 14538	5 ppm

Total Ash Exposure from B20 at 435k miles ~ 670 grams

- Alkali and alkaline earth metals can be detrimental to DPF durability and performance
  - Alkali attack on SiC protective oxide coating (1)
  - CaO will act as a sintering aid for cordierite (2)
  - Accumulated ash will increase backpressure of wall-flow DPF (3)
  - Biodiesel can degrade mechanical properties (4)
- **What is the impact of metal impurities on the durability of the DPF?**

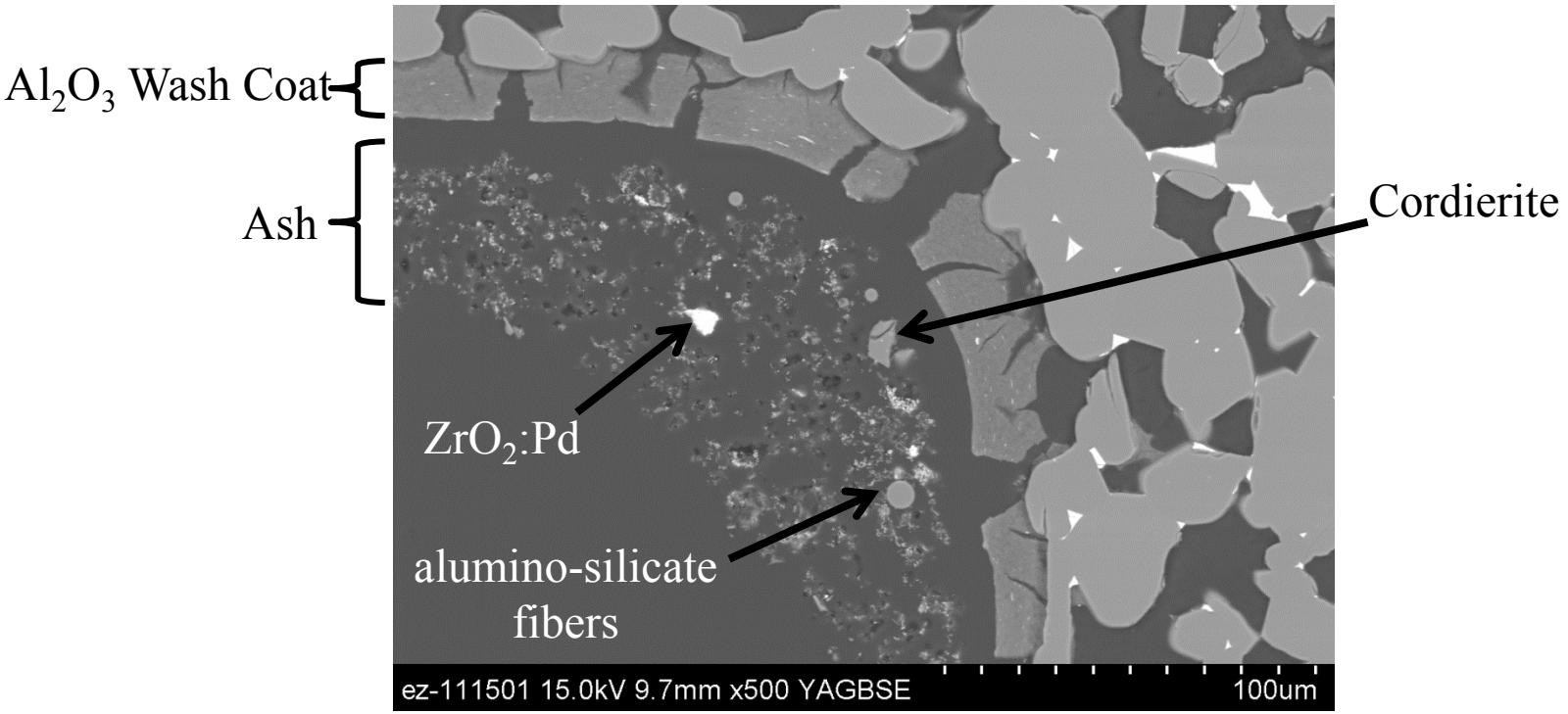
(1) Choi, et al., SAE 2007-01-1939, (2) Chen, J. of Alloys & Comp. 455 (2008) 298–302, (3) Sappok, Wong, SAE 2010-01-0811, (4) Williams, et al., SAE 2011 01-1136.

DPF Accelerated Aging Test (Conducted at NREL)

- Aging full production exhaust systems from 2011 Ford F250 pickup
- 4 separate tests were conducted. ULSD, B20 + 14ppm Na, B20 + 14ppm K and B20 + 14ppm Ca
- Aging conducted on Cat C9 engine
- 100 hour test simulated 150k miles of operation on SiC DPF
- A three-mode, one-hour test cycle was developed for catalyst aging (suggested by Ford).
  - 15 minutes @ 200 C (Low Temp), 15 minutes @ 340 C (High Temp), and 30 minutes @ 700 C (Regen).

Microstructural, Chemical and Mechanical Analyses of Biodiesel Aged DPFs is being Conducted

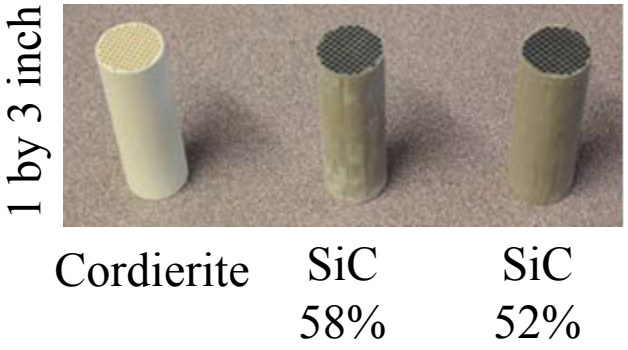
B20 + Na Additive after simulated 150,000 miles (1 cm from outlet)



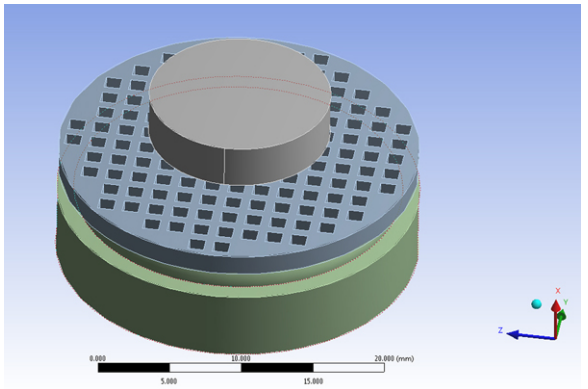
- Ash doesn't show any penetration into the SiC.
- Ash was observable on the wall but no ash plugs observed.
- Analysis of these samples is ongoing.

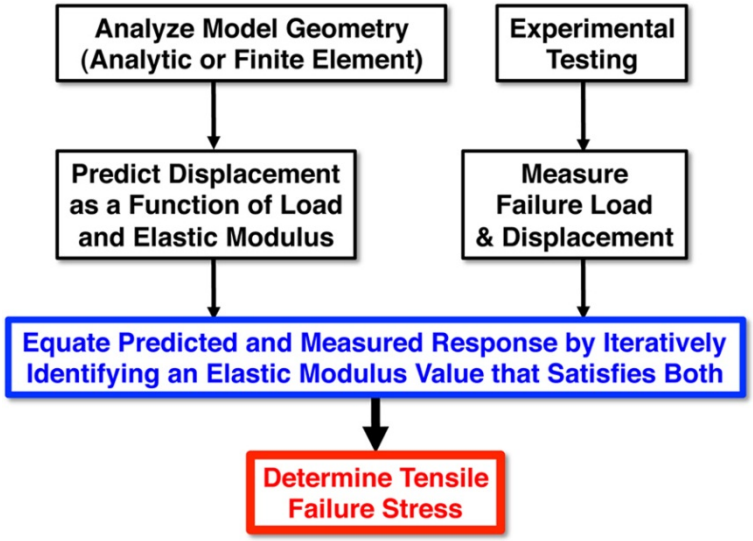
Mechanical Testing of DPF specimens

Mechanical properties may be the most sensitive indicator of the onset of degradation.



Solid model of a DPF biaxial flexure disk





Material	Cordierite	Cordierite	SiC	SiC
Porosity (%)	59	59	52	58
Pore Size (µm)	18	13	23	23
Measured				
Fracture Load (N)	2.78	3.06	11.72	9.57
Displacement (µm)	38	17.2	38.3	33
Calculated using ANSYS				
Young's Modulus (GPa)	2.7	6.6	11.3	10.5
1st Prinicpal Stress (MPa)	3.5	3.8	14.5	11.9

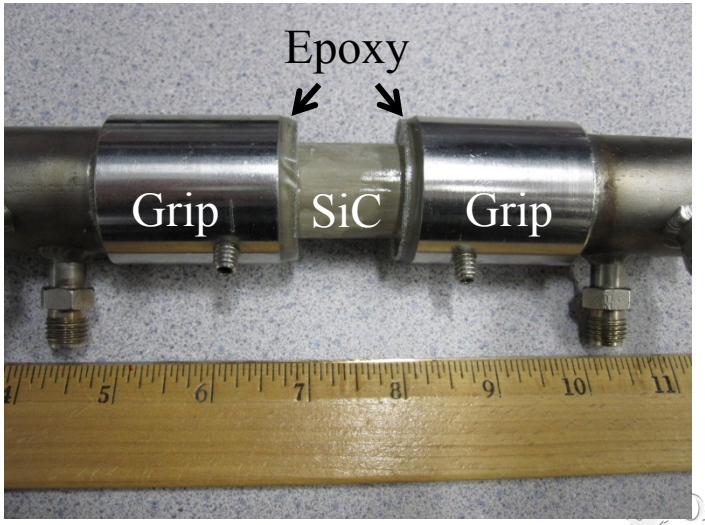
New Approach: Tensile Testing of DPF Specimens

- New method based on applying tensile load through epoxy will be used to measure fracture strength and elastic modulus.
- Advantages of tensile testing over flexure
  - Reduction/elimination of role of surface damage in failure initiation.
  - Generation of entire tensile-stress vs. tensile-strain curve, and therefore, also the generation of (tangent) modulus as a function of tensile strain up to failure.
  - Samples a much larger effective volume and effective area.

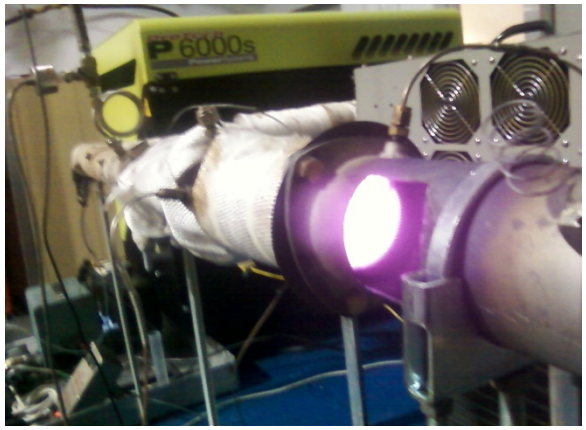
$$R_s = \frac{\kappa \sigma_f (1-\nu)}{\alpha E}$$

R_s = thermal shock resistance
κ = thermal conductivity
σ_f = tensile fracture strength
ν = Poisson's ratio
E = elastic modulus
α = coefficient of thermal expansion

Epoxy Mounted 1X3 inch SiC DPF

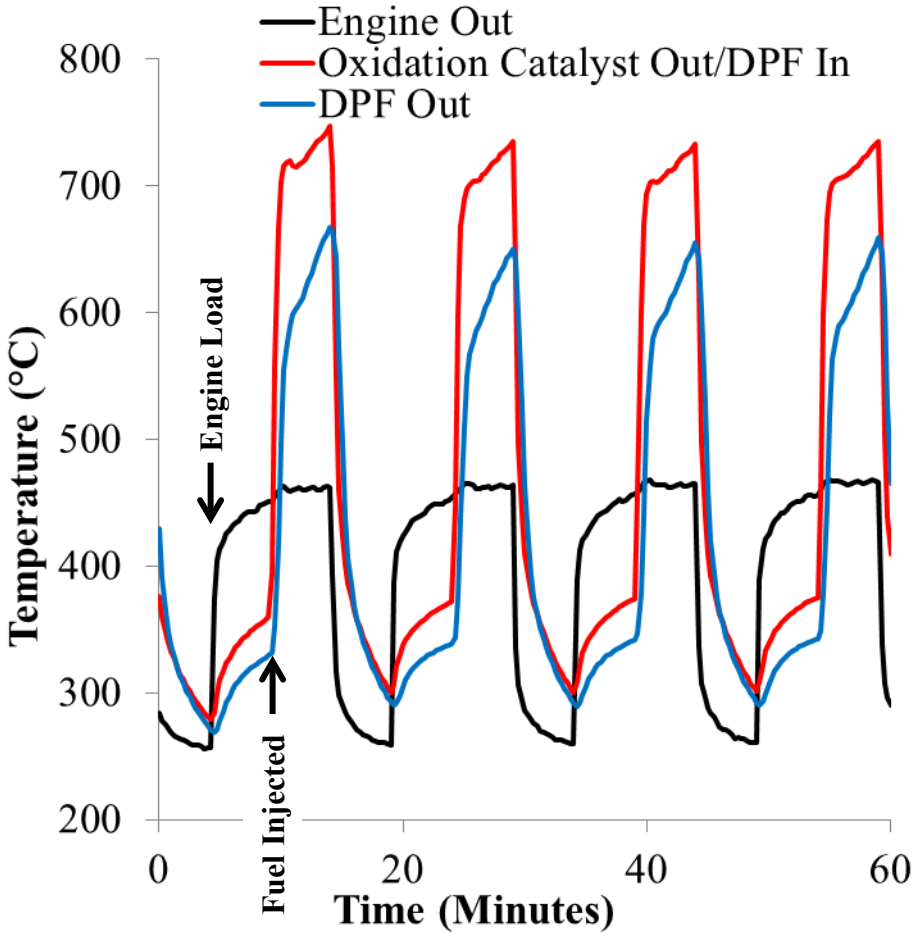


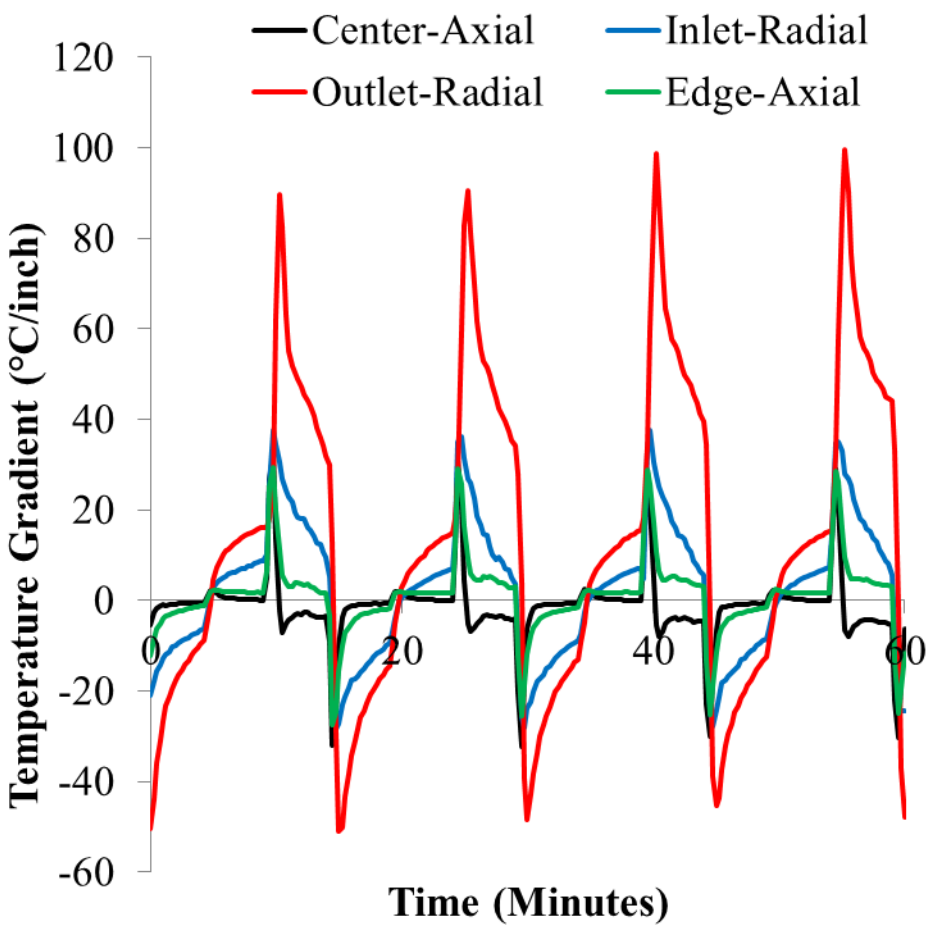
Diesel Gen-Set for 24/7 DPF Regeneration Cycling



- Pramac P6000S silenced diesel gen-set has been installed at the NTRC (National Transportation Research Center) building at ORNL. The engine is 10 hp and is rated for 4800 W and is connected to an Avtron K490 load bank.
- Shakedown testing indicated the need for a complete change of exhaust system due to the use of a glass-pack muffler which shed fibers and face-plugged the DPF and due to excess cooling of exhaust, which was done by the manufacturer for safety of outdoor installations.
- Thermal cycling of the diesel particulate filter is done by a combination of gen-set load and exhaust fuel injection and can reach temperatures up to 1200ºC in a 15 minute cycle.

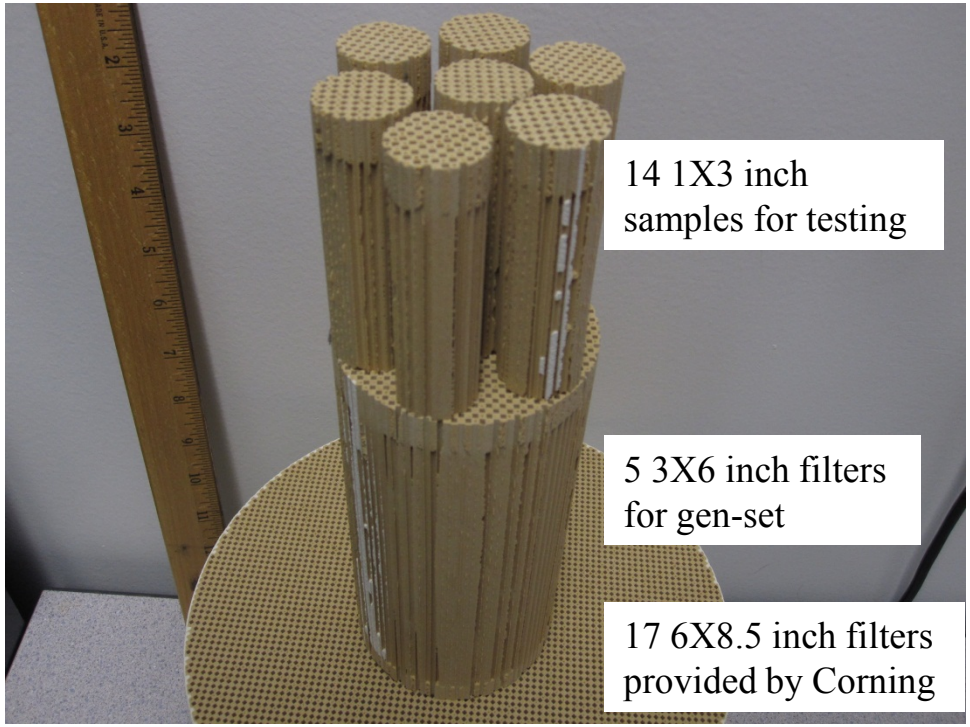
First Sample Tested for 106 cycles on gen-set using ULSD





- Largest temperature gradient is at the outlet between the center and the edge.
- Gen-set allows for cheaper and more versatile cycling.

Cordierite filters for Accelerated Aging



- A lathe is used to machine suitable test specimens out of the as-received DPF bricks.
- 14 testing specimens can be obtained from each 3X6 inch filter which will be enough for statistical analysis.
- Mechanical properties can be measured radially and axially.

Collaborations

- Ford Motor Company
- National Renewable Energy Laboratory (NREL)
- Manufacturers of Emission Controls Association (MECA)
- National Biodiesel Board (NBB)
- Samples provided by Corning

Future Work

- Collaboration with Ford, NREL, MECA and NBB will continue with analysis of accelerated biodiesel-aged specimens.
- Tensile testing of DPF samples using epoxy mounting will continue to be developed.
- Baseline measurements of DPF mechanical properties changes due to regeneration using ULSD will be conducted.
- Incremental accelerated aging with Na, K and Ca dosing in order to simulate long-term biodiesel (B20) exposure will be conducted with gen-set and subsequent DPF material degradation will be measured.

Summary

Relevance

Will biodiesel negatively impact DPF performance?

Approach

Accelerated aging with (1) NREL/Ford and (2) at ORNL.

Technical Accomplishments and Progress

- Low temperature corrosion was likely caused by biodiesel attack of the polymeric binder holding the skin together.
- Finite element based approach whereby mechanical properties are determined by iteratively comparing experiment results with FEA properties was established.
- Long-term low-cost testing of materials in real diesel engine exhaust was established at NTRC.

Collaboration with NREL, Ford and MECA on biodiesel aging was established.

Proposed Future Work

Gen-set will be used to conduct accelerated biodiesel aging in order to determine the effect of metal additives on DPF material properties.