Non-Petroleum-Based Fuels: Effects on Emissions Control Technologies

Scott Sluder, John Storey,
Todd Toops, Stuart Daw,
Andrea Strzelec, Sam Lewis,
Bruce Bunting, Michael Lance

Oak Ridge National Laboratory

DOE Management Team:
Kevin Stork, Dennis Smith,
and Drew Ronneberg

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE National Laboratory

Project Overview

Timeline

- Project is ongoing but re-focused each year to address current DOE and industry needs.
  - FY10 start: Lean-Ethanol LNC
  - FY09 start: Biodiesel-based Na
  - FY08 start: EGR cooler fouling
  - FY07 start: PM kinetics + chemistry

Barriers

- Inadequate data and predictive tools for fuel property effects on:
  - combustion and engine optimization
  - emission control system impacts.

Budget

- Funding received in
  - FY09: $845K
  - FY10: $1100K allocated to date
- Anticipate similar or lower funding level for FY11.

Partners

- Collaborators and their roles
  - CLEERS: evaluation protocols
  - Cummins/Ford/GM: experimental guidance
  - NREL/GM/MECA: Biodiesel-aged emissions control devices
  - Research Personnel
    - Penn State University
    - University of Tennessee
    - University of Wisconsin

Objectives and Relevance

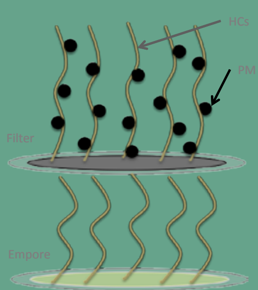
If NPBF effects can be understood and accounted for, they can be introduced at higher blending levels.

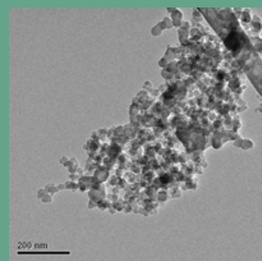
<u>Project Goals:</u> Provide data in support of predictive tools that can be used to understand fuel-property impacts on combustion and emissions control systems.

- **Non-petroleum based fuels are relatively new and not fully understood.**
- **Current vehicles are sophisticated and can be sensitive to fuel formulations.**
- **Industry is hesitant to implement new fuels and formulations because systems could fall out of specification.**
- **Research is aimed at determining effects of new NPBF formulations.**
  - **Compare to standard fuel formulations**
    - **Biodiesel vs. ULSD**
    - **Ethanol vs. gasoline**

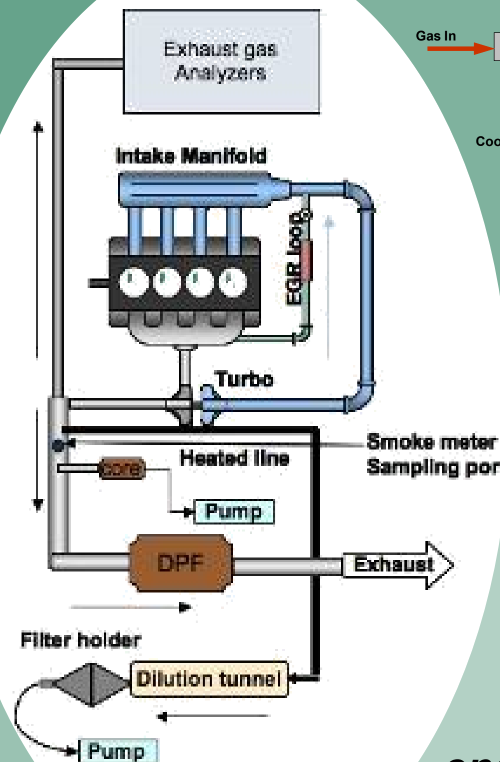
Approach

Bring together targeted, engine-based and bench reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand behavior for specific technologies.

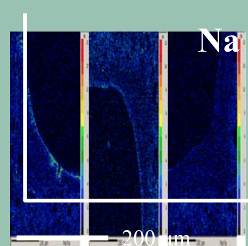




Study fuel- and engine-specific PM to support reduced fuel penalty for emissions control.



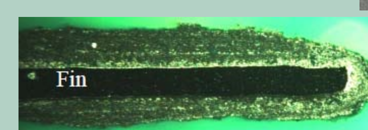
Enable examination of EGR cooler deposits to support models and component development.



Identify specific Na-related impact for each emissions control device.

New characterization techniques are key to these activities.

Collaborations enable comparisons to real world, full size devices.



Milestones for FY 2010

- Establish EGR cooler performance and degradation metrics. ($300K)
  - Focus on renewable fuel blend and its base stock
  - Study under controlled transient conditions.
- Complete study for biodiesel-generated PM and publish derived kinetic parameters in open literature. ($300K)
- Complete and report on methods to isolate corrosive compounds in ethanol combustion products. ($400K)
- Identify emissions control impact of 5 ppm levels of Na in Biodiesel over vehicle lifetime ($250K)
  - Initiate rapid aging study and implementation; Corroborate with field aged devices
  - Characterize and evaluate devices for materials and performance impact.
- Complete kinetic study of Ag-based lean NOx catalysis system based on lean burn ethanol-fueled vehicle. ($200K)
  - Kinetic parameters include: NOx reduction activity, activation energy, and reaction orders of key reactants.

Summary of Technical Accomplishments

- **Verified B20 produces EGR cooler fouling similar to ULSD but results in higher HC levels in deposits.**
  - Based on these findings, a study was initiated on HC role in fouling.
  - Initial results indicate HCs concentrated at cooler wall.
- **Identified dependence of surface area and developed a model for particulate matter oxidation**
  - Showed B100-generated particulate oxidizes at lower temperatures due to increased surface area
  - PhD awarded at University of Wisconsin (Andrea Strzelec)
- **Demonstrated collection of exhaust condensates for analysis of organic and inorganic acids by capillary electrophoresis chromatography.**
- **Completed initial characterization and performance analysis of Na-impact on DOC, LNT, DPF, and SCR emissions control devices**
  - Engine-aged emissions control devices operated with B20
  - Accelerated Na-aging effort with DOC/SCR/DPF system
- **Initiated study on Lean NOx Catalyst study for ethanol fueled vehicles; established collaboration with Galen Fisher and secured commercial catalyst**

NPBF Effects on EGR Cooler Fouling

NPBF Effects on EGR Cooler Fouling

Does use of biodiesel blends and other non-traditional fuel formulations cause worse cooler fouling than with ULSD?

Benefit: Improved understanding of EGR cooler fouling processes will enable better models and reduces impacts of fouling.

- Reduces aftertreatment cost
- Improves engine system efficiency

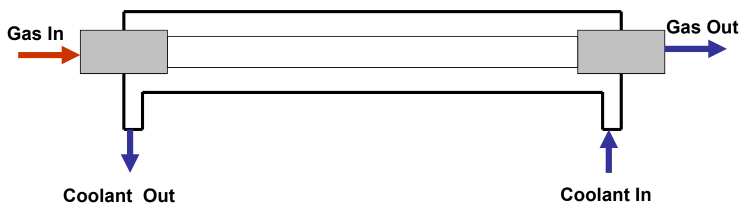
Accomplishments: Completed initial experiments aimed at investigating how HCs play a role in the fouling process.

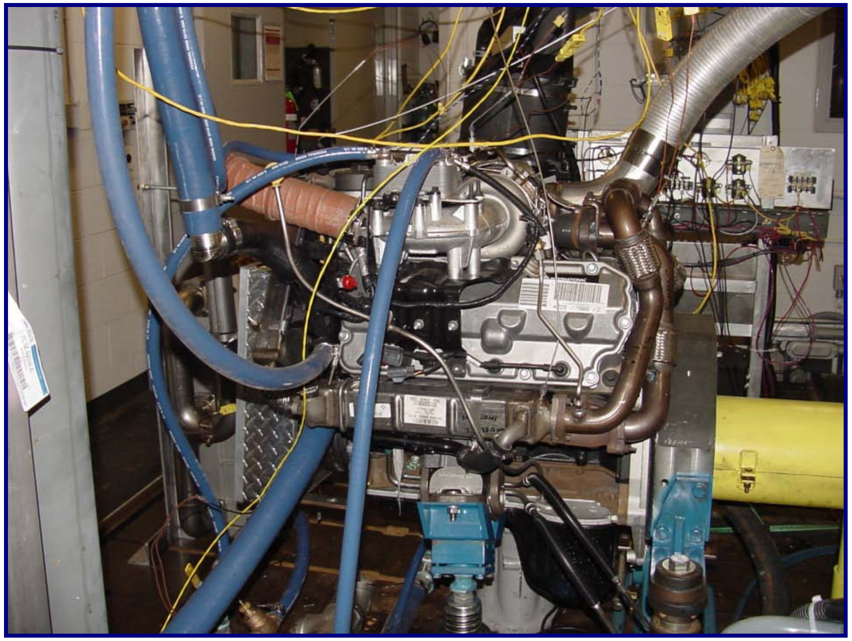
- Results suggest that under most conditions, HCs are present near the cold wall.
- Efforts to determine when HCs can play a more substantial role are ongoing; the goal is to identify conditions where HCs are problematic.
- A means of rapidly determining the fraction of HCs in the exhaust that are of concern to fouling is being developed.

NPBF Effects on EGR Cooler Fouling

Surrogate EGR cooler tubes are employed to enable multiple analyses of deposits.

- Ford 6.4-L V-8 used as exhaust generator.
- Surrogate tubes provide more accessible samples for study than full-size coolers.
  - Earlier effort (FY08) demonstrated approach replicates full size devices.
- Exhaust passed through surrogate EGR cooler tubes at constant flow rate and coolant temperature.
  - Tubes were ¼ inch square cross-section stainless tubes.
  - Thermal effectiveness of tubes is assessed during exposure.
- Subsequent analyses of tube deposits:
  - Total mass of deposits
  - Volatile / non-volatile deposit mass
  - GC/MS characterization of the deposit HCs
  - Deposit layer thermal properties



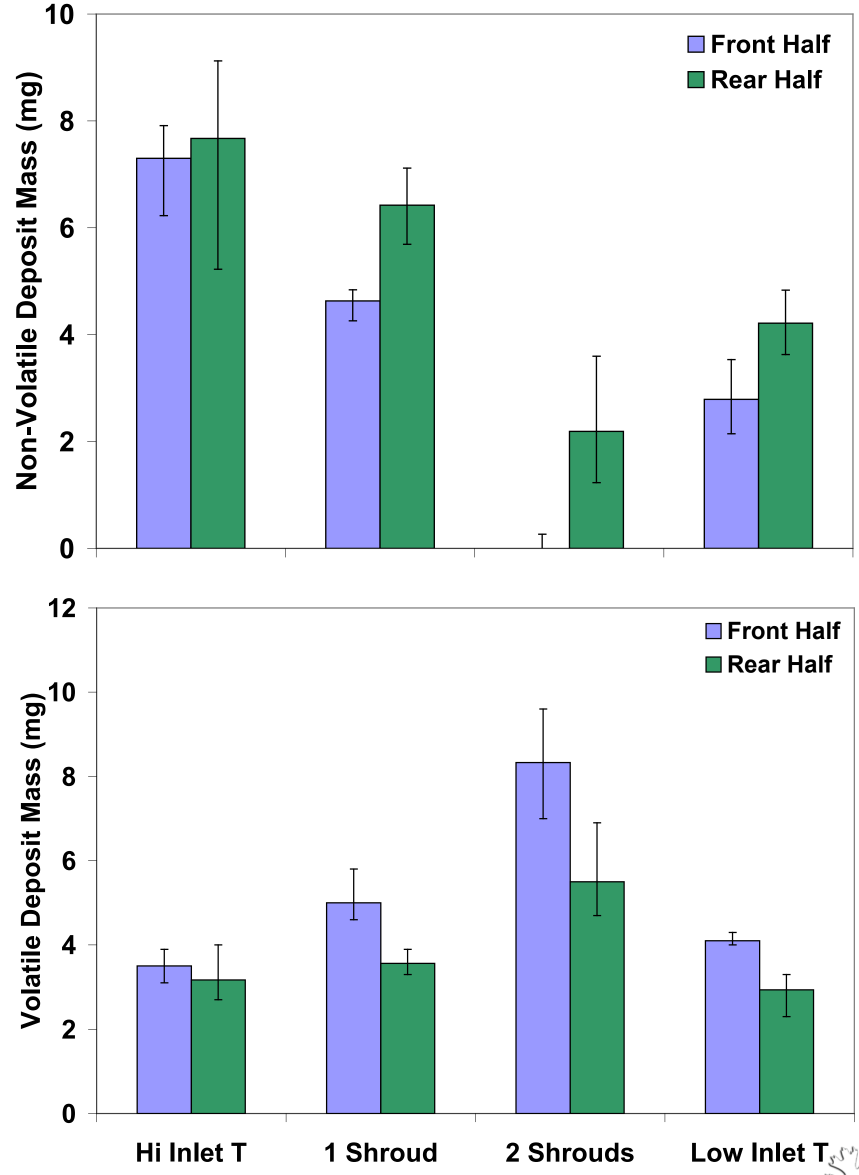


NPBF Effects on EGR Cooler Fouling

To date, data continues to suggest most operational conditions result in HCs only near the tube wall, not near the deposit/gas interface.

- **Series of experiments varied gas inlet and deposit surface temperature to check for deposit mass variation.**
  - **Plastic shrouds on coolant side allow variation of surface temperature.**
  - **Tubes analyzed in sections to check for HC and soot nonuniformity.**

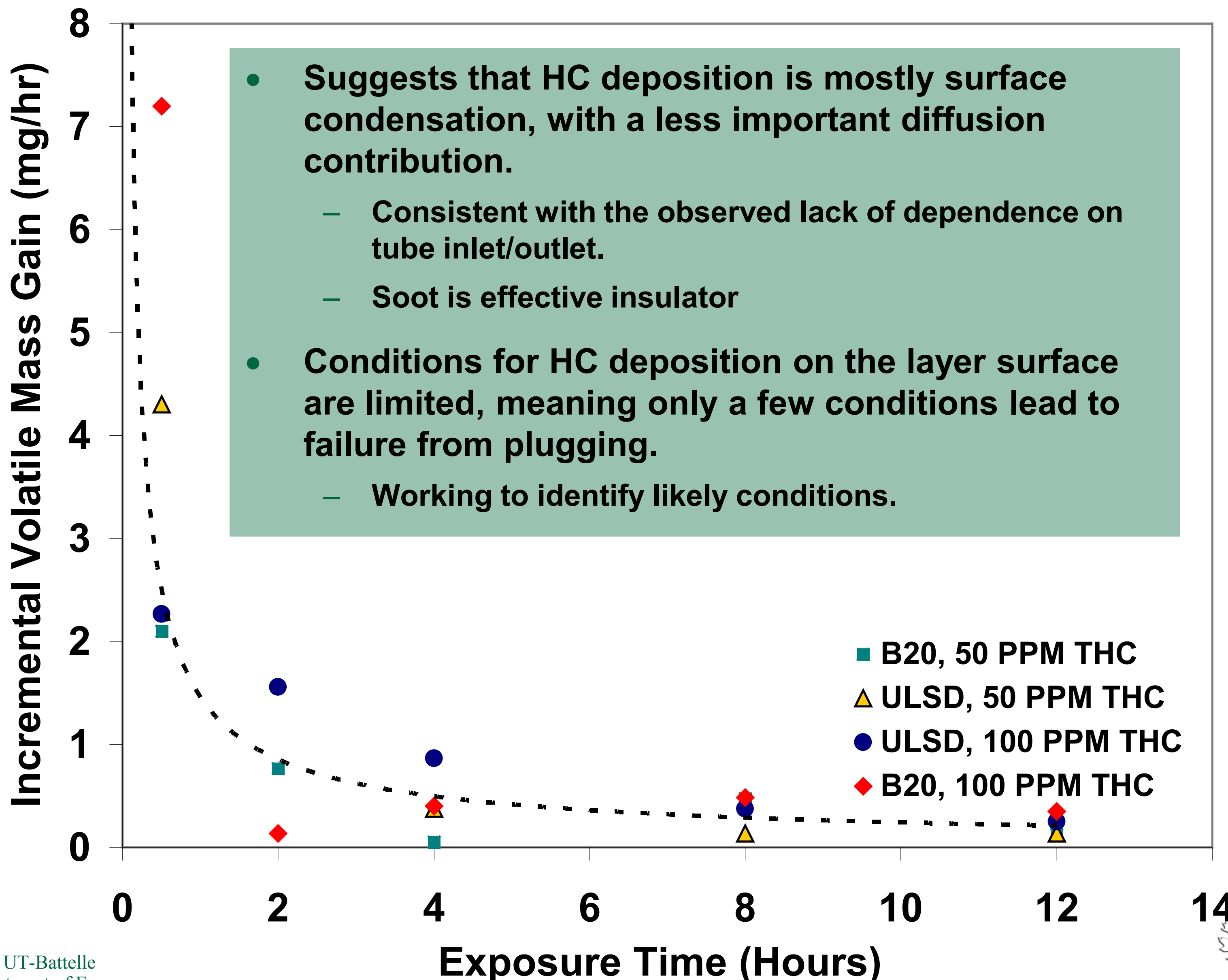
Results suggest a uniform deposit along the tube length. They also continue to suggest that HCs are mostly limited to an area of the deposit near the cold tube wall.



NPBF Effects on EGR Cooler Fouling

Time-series experiments reveal that the rate of deposition of volatiles is high when the deposit layer is thin, but drops rapidly as the layer thickens.

- Suggests that HC deposition is mostly surface condensation, with a less important diffusion contribution.
  - Consistent with the observed lack of dependence on tube inlet/outlet.
  - Soot is effective insulator
- Conditions for HC deposition on the layer surface are limited, meaning only a few conditions lead to failure from plugging.
  - Working to identify likely conditions.



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NPBF Effects on Particulate Matter (PM) Oxidation

NPBF Effects on PM Oxidation Kinetics

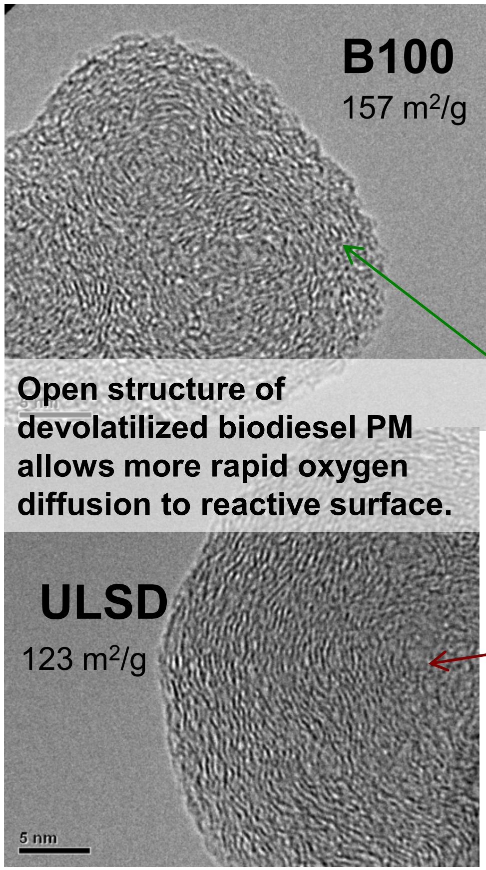
Objective: Measure and model impact of biodiesel fuel blending on oxidation reactivity of exhaust particulate matter.

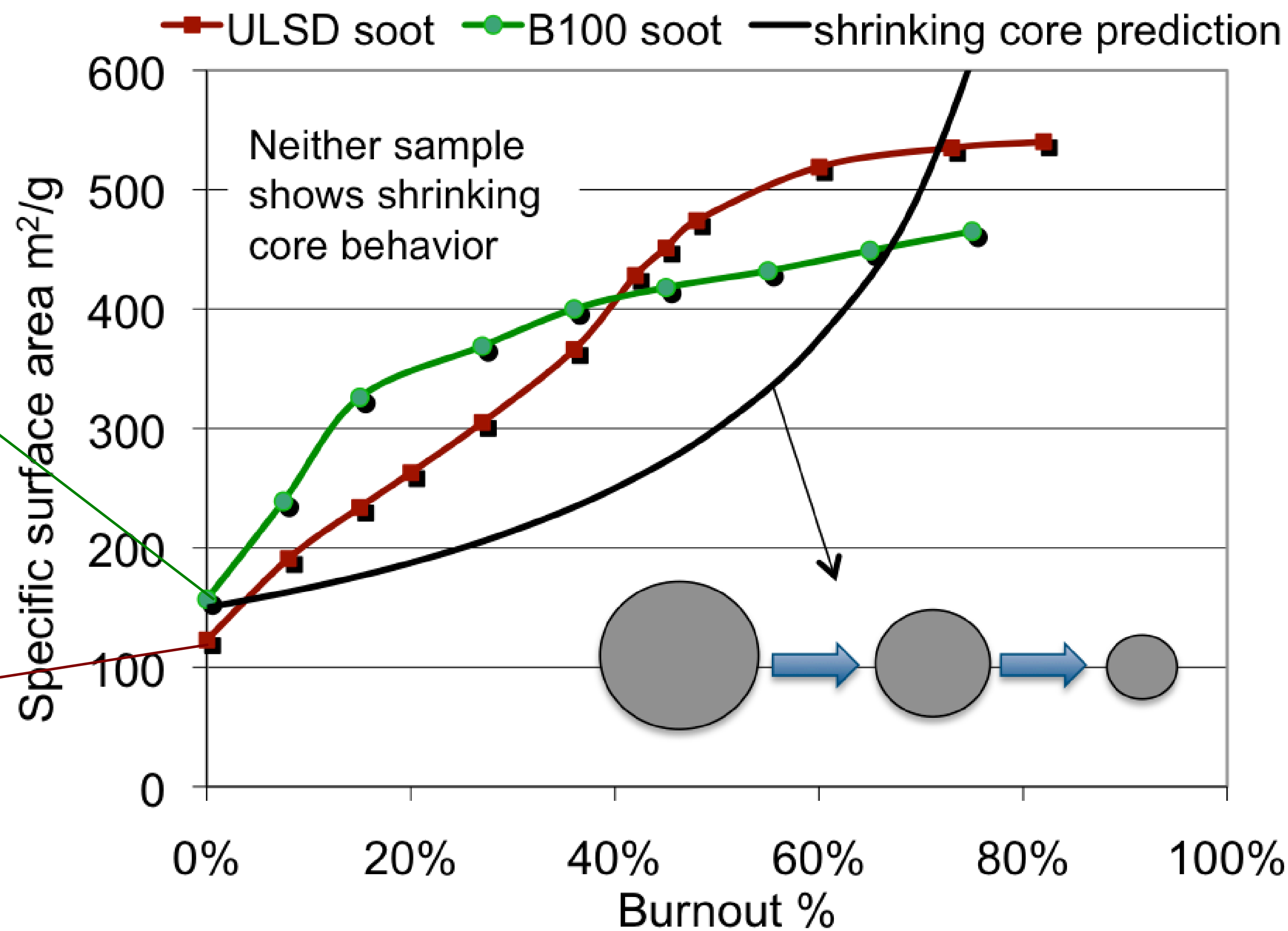
Benefit: Improved understanding of biodiesel PM reactivity differences will enable more fuel-efficient regeneration of diesel particulate filters (DPFs).

Accomplishments:

1. Identified role of devolatilized surface area in fixed carbon oxidation.
2. Developed model for combined devolatilization and fixed carbon burnout.
   - Microstructural differences in conventional and biodiesel PM lead to differences in oxidation reactivity (FY09).
   - PM from high biodiesel fuel blends (> B10) contains higher volatiles.
     - Higher volatile level correlates with lower ignition temperature.
   - PM surface area evolution with burnout directly correlates to oxidation rate.
     - B100 PM has higher initial surface area.
     - Shrinking core behavior not observed for either low or high biodiesel PM.
   - Combined PM oxidation model accounts for both volatiles and fixed carbon.

Biodiesel content impacts particle morphology and evolution of fixed carbon surface area.

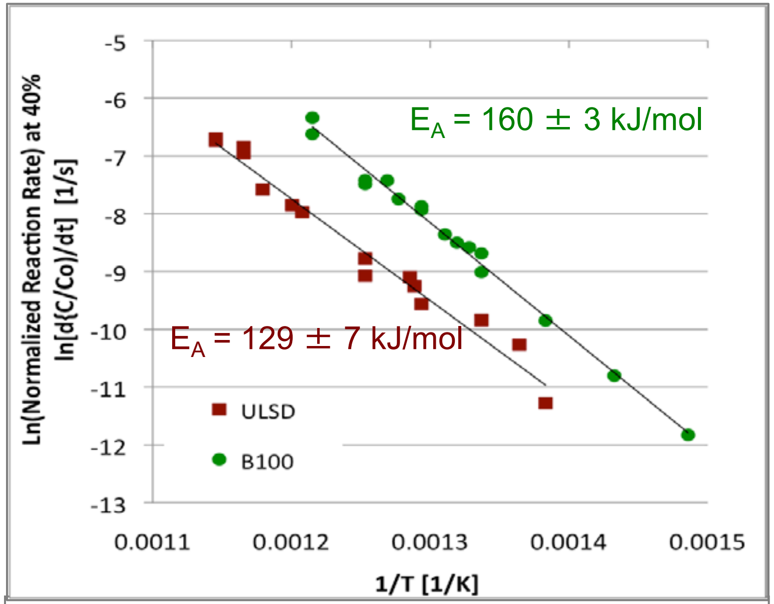




For the first 40% of the burnout, the biodiesel PM has significantly greater surface area as compared to ULSD PM.

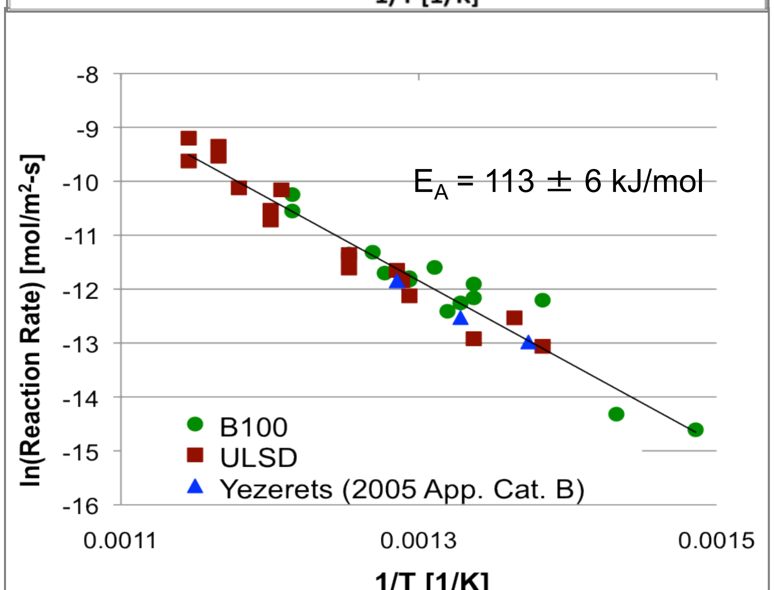
NPBF Effects on PM Oxidation Kinetics

Normalizing fixed carbon oxidation rates to available surface area, allows oxidation kinetics to be described by single activation energy.



Rate of fixed carbon oxidation at 40% burnout.

$$\frac{\text{Measured Rate of } CO_2 \text{ formation [mole/s]}}{\text{Initial Carbon [mole]}}$$



Rate of fixed carbon oxidation normalized to instantaneous surface area for entire range of burnout.

$$\frac{\text{Measured Rate of } CO_2 \text{ formation [mole/s]}}{\text{Instantaneous surface area } [m^2]}$$

NPBF Effects on PM Oxidation Kinetics

PM oxidation model shows good agreement with experiments.

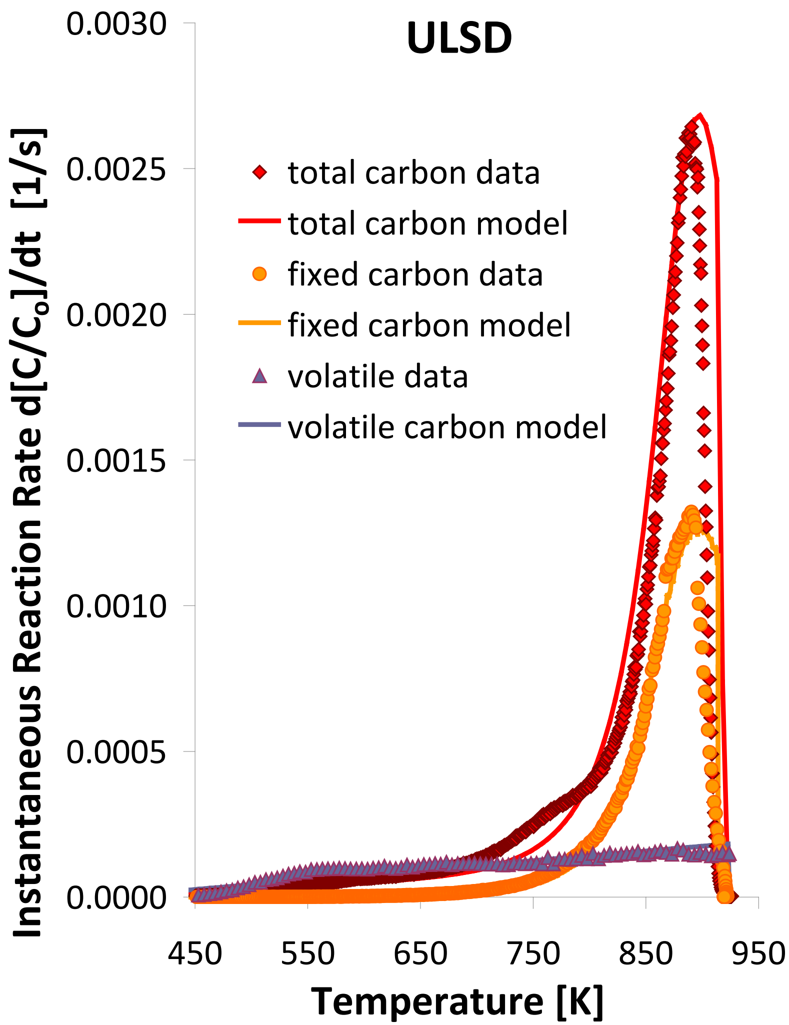
Combined oxidation kinetics for diesel PM:

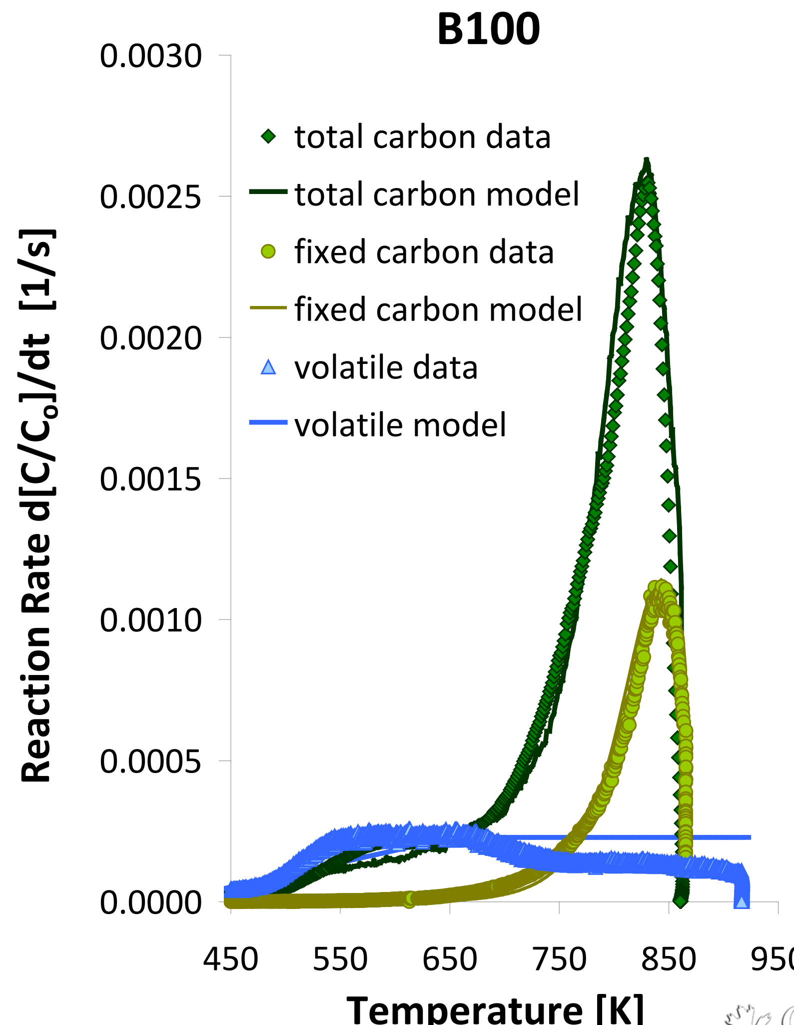
$r_{total} = r_{volatiles} + r_{fixed\ C}$ [moles/s]

net rate of C loss = loss of volatile C + loss of fixed C

$r_{volatiles} = f(T) X_{volatiles} m_{C,o}$ [moles/s]

$r_{fixed\ C} = k[C]/(SA_{specific} * m_c)$ [moles/s]





NPBF Effects on Emissions Control Devices

NPBF Effects on Emissions Control Devices

Is <5 ppm Na specification for biodiesel sufficient to ensure performance of emissions control devices over the vehicle lifetime?

Benefit: Identify potential problem areas that would limit the introduction of biodiesel at higher blend levels than B5 (5% biodiesel + ULSD).

- Efforts will aim to determine if problems exist and investigate mitigation strategies, if necessary.

Accomplishments:

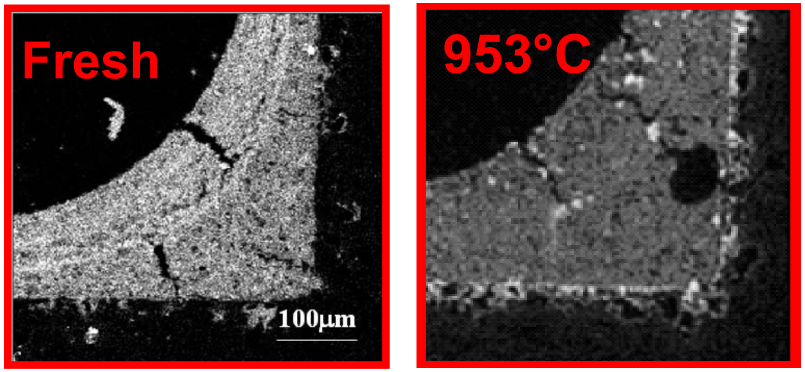
1. Completed initial analysis of engine-aged parts that we received from our collaborators (DOC+DPF system and LNT)
   - Na detected in DOC and LNT parts, but performance not impacted
   - Na- and Ca-based ash accumulation observed in DPF plug; 20:1 Ca:Na
2. Completed initial accelerated Na-aging effort with DOC/SCR/DPF system
   - SCR performance is significantly impacted

Na exists in Biodiesel at trace levels due to the synthesis process and could effect emissions control devices

- NaOH or KOH is a liquid-phase catalyst used in biodiesel synthesis
  - NaOH and KOH difficult to separate completely from products
  - Specification set at 5 ppm Na/K
- Anecdotal reports of accelerated ash accumulation with biodiesel use
  - Up to 2 times faster ash accumulation?
- Alkali absorption into monolith walls and possible weakening of monolith
  - K and Na would have similar impact
- Zeolite/SCR poisoning (NOx reduction)
  - Na/K can adsorb/exchange on active sites in SCR catalysts

Ash plugs

K migration into cordierite



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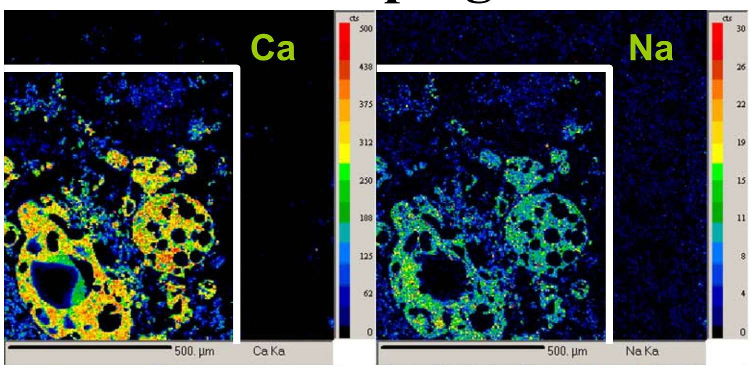
Ash plugs observed in DPF operated with B20 are primarily comprised of lube oil-based Ca not biodiesel-based Na

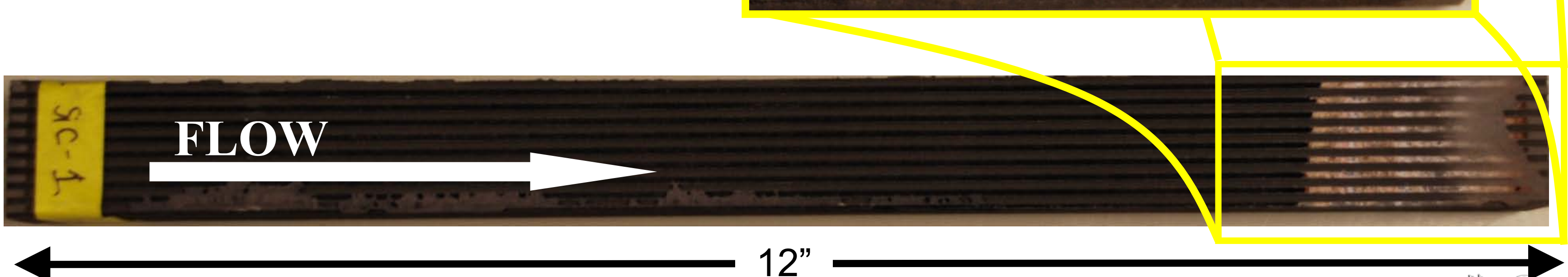
DPF operated for 120,000 miles with B20 that was within specification. A DOC was used upstream.

- **Ash plugs apparent in rear of DPF**
- **20x more Ca than Na detected in ash**
  - Ca associated with standard lube oil
  - IF increased ash accumulation does occur w/ B20, it is probably due to:
    - Out of spec biodiesel, or
    - Increased oil consumption
- **Minimal Na detected in wall of DPF**

EPMA of ash plugs in DPF

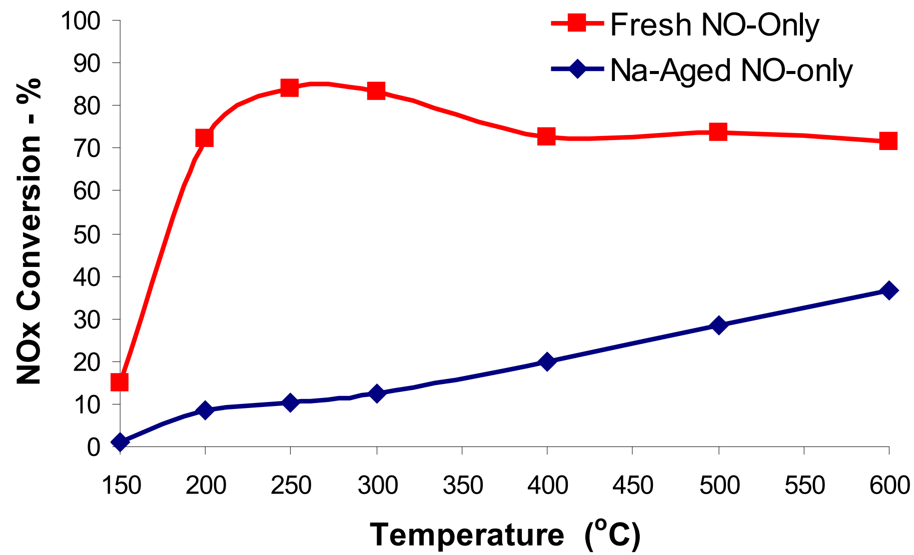


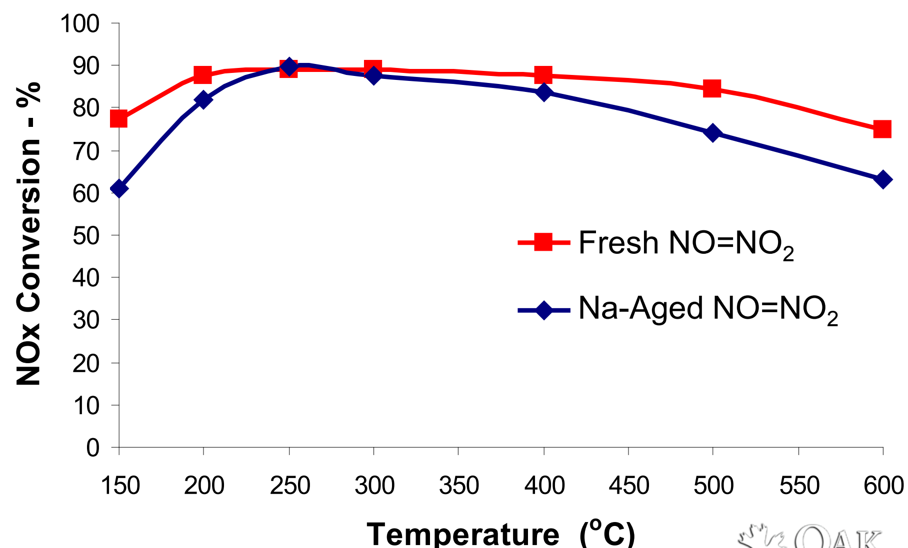
Ash plugs in exposed DPF channels



Initial accelerated aging approach on DOC→SCR→DPF system reveals impact in SCR performance with Na addition

- **Single cylinder engine at constant load with high Na content**
  - **Periodic soot regeneration; T_{avg}=650°C**
- **Highly elevated Na-levels to achieve 435,000k mile equivalent Na (5 ppm basis)**
  - **5000+ ppm Na and S in B20**
- **DOC/SCR/DPF system**
- **SCR performance measured on bench reactor with aged core**
- **NO-only performance evaluation is greatly impacted**
  - **When $NO=NO_2$ impact is minimal**
  - **Points to site specific deactivation**





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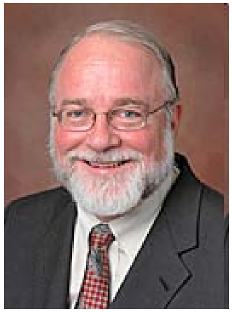
Collaborators and Partners

- **NPBF Effects on EGR Cooler Fouling**
  - Ford/GM: experimental guidance
- **NPBF Effects on PM Oxidation Kinetics**
  - Penn State University: microscopy and PM structural analysis
  - University of Wisconsin: graduate research
  - NREL: performed limited oxidation study of PM generated in their biodiesel blend program
- **NPBF Effects on Emissions Control Devices**
  - NREL/GM/MECA: Biodiesel-aged emissions control devices
  - University of Tennessee: graduate research conducted at
  - CLEERS: evaluation protocols
- **Lean NOx catalysis for ethanol fueled vehicles**
  - Galen Fisher will provide commercially relevant catalysts and serve as a technical advisor
    - Formerly of Delphi, now Adjunct Professor at Univ. Michigan



Future Directions (Beyond FY10)

- **Future EGR efforts will focus on identifying linkages between HCs and deposit layer stability with the goal of exploring opportunities for fuel formulation changes to reduce deposit stability (and hence reduce fouling).**
- **Soot oxidation kinetics work will continue to be expanded to explore oxidation kinetics with NO_2**
  - **Extend collaboration with Penn State University; sponsor graduate research that will be performed at both PSU and ORNL**
- **Analytical development will continue to improve methods for analysis of soot and condensable exhaust species that affect system performance.**
- **The Na impact study will continue with investigation into SCR impact and try DOC/DPF/SCR arrangement with accelerated approach.**
  - **Continue to work closely with NREL/MECA to obtain and characterize aged biodiesel and ULSD emissions control devices.**
  - **Oil dilution from biodiesel also a concern; plan to incorporate into study.**
- **Lean NOx catalyst effort will complete initial kinetic study then start including additional reductants for synergistic effects.**
  - **Goal is to build model to be used with E85 and validate on a vehicle**
- **As always, we welcome specific concerns from industry, whether in these areas or other topics, for future studies.**

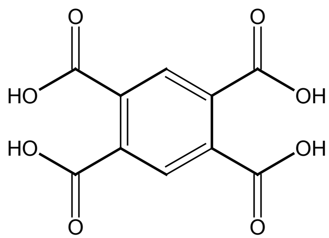
Summary

- Relevance: This project is targeted towards providing data and predictive tools to address gaps in information needed to enable broad use of NPBFs. (DOE Technical Barrier)
  - If NPBF effects can be understood and accounted for, they can be introduced at higher blending levels.
- Approach: The approach being pursued is to bring together targeted, engine-based studies using NPBFs with in-depth characterization of PM and HCs to better understand behavior for specific technologies. (Currently emissions control devices and EGR Systems)
- Collaborations: with several industry stakeholders and universities are being used to maximize the impact of this work.
- Technical Accomplishments:
  - NPBF effects on EGR cooler shown to increase HC-level; HCs concentrated at wall.
  - PM oxidation model developed based on surface area evolution; accounts for HCs.
  - Biodiesel-based Na detected in all emissions control devices, but only shown to impact SCR performance to date
- Future Work: plans are in place; industry input towards those plans or other NPBF-emissions control effect concerns is needed and welcomed.

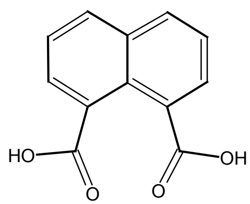
SUPPLEMENTAL SLIDES

Exhaust condensates critical to aftertreatment components

Aromatic acids found in EGR cooler soot



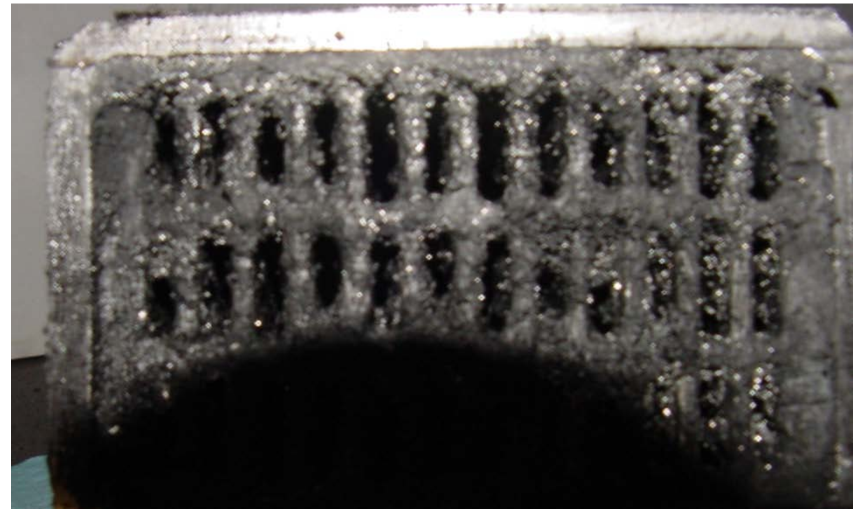
1,2,4,5-Benzenetetracarboxylic acid (and related dianhydride)



1,8-Napthalene-dicarboxylic acid (and related annhydride)

Condensates include:

H_2SO_4, HNO_3, $HCOOH$, CH_3COOH



- **Exhaust can condense in EGR coolers or charge air coolers**
- **Acids stay in condensate; sulfuric, nitric, formic and acetic acids are the most common**
- **pH can be very low for some condensates (pH < 3)**
- **Biofuels will tend to produce more organic acids leading to potential corrosion and gumming issues.**

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