Fuel Effects on Emissions Control Technologies

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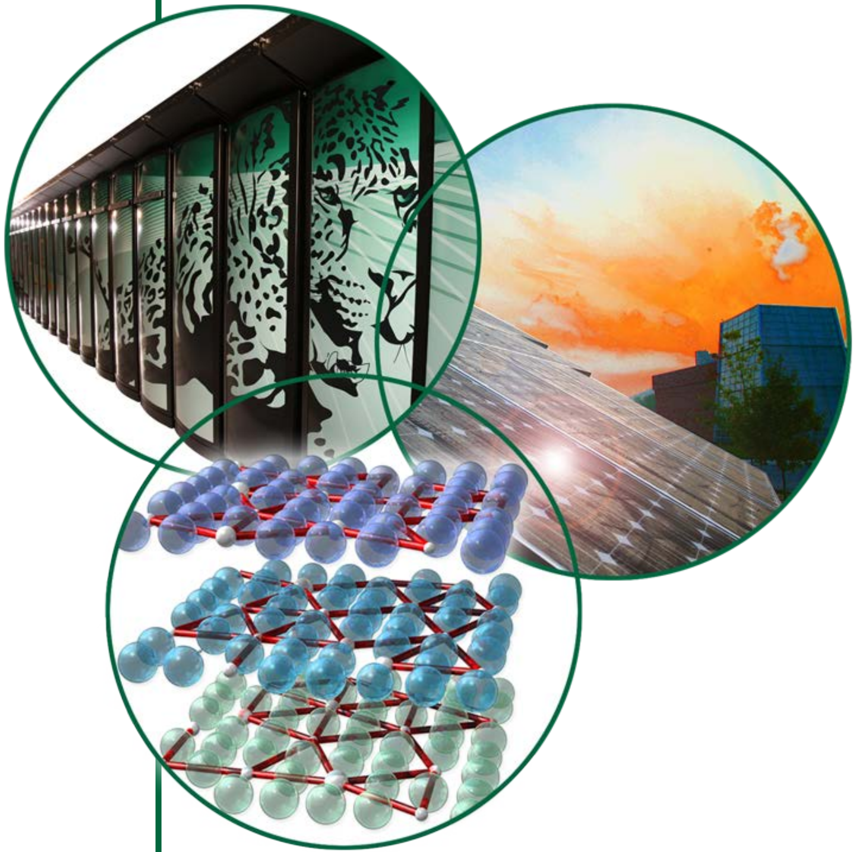

2012 DOE Annual Merit Review

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U.S. DEPARTMENT OF ENERGY

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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 effects on emissions and emission control system impacts. (2.4 D)**
- **Inadequate data on long-term impact of fuel and lubricants on engines and emissions control systems. (2.4 E)**

Budget

- **Funding received in**
  - **FY11: $725K**
  - **FY12: $1,065K (expected)**

Partners

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

Objectives and Relevance

Objective: Provide data in support of predictive tools that can be used to understand fuel-property impacts on combustion and emissions control systems.

Relevance: Addresses Fuels Technology barriers D and E: Inadequate data and predictive tools for fuel effects on emissions and emission control system impacts and inadequate data on long-term impacts of fuel and lubricants on engines and emission control systems.

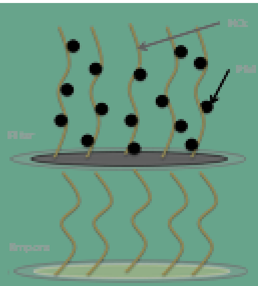
Changes in fuel properties, whether caused by emerging fuel sources or increasing blend levels, can have unintended and undesirable impacts on increasingly complex vehicles.

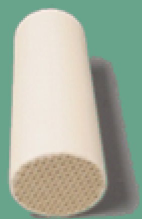
Milestones for FY 2012

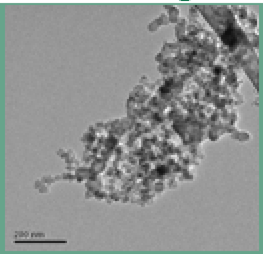
- **Establish EGR cooler performance and degradation metrics. ($300K)**
  - Investigate low-temperature deposit formation characteristics.
  - Determine whether velocity-induced shear forces can remove deposits.
- **Determine key reactions for NO_X reduction over silver-alumina catalyst. ($200K)**
- **Determine sodium, potassium, calcium impact on DOC-DPF-SCR system. ($300K)**
- **Investigate soot reactivity relationships with engine operational parameters. ($75K)**
- **Assess Properties, Emissions, and Compatibility of Emerging Fuels. ($190K)**
  - Implement a pyrolysis-GC/MS capability to enable improved study of fuel and lubricant impacts on soot characteristics and catalyst poisoning.

Approach

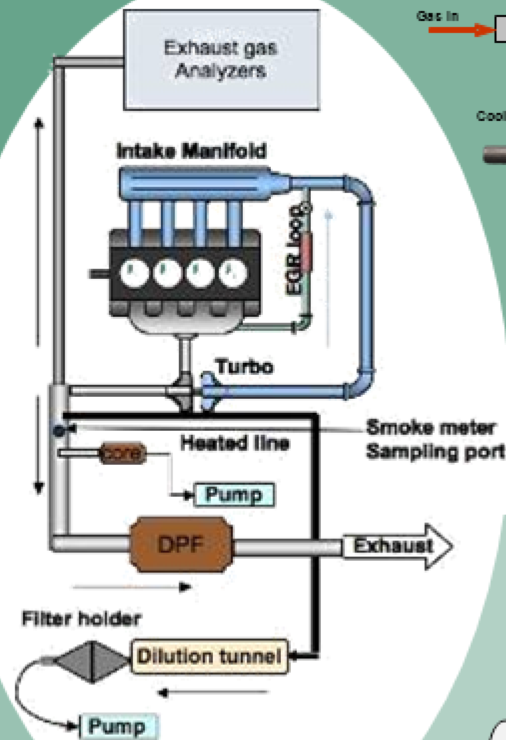
Bring together targeted, engine-based, micro-reactor, and bench reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel interactions with emissions control components.

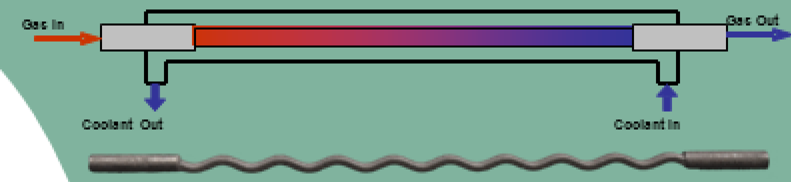




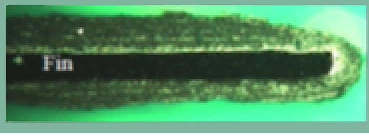


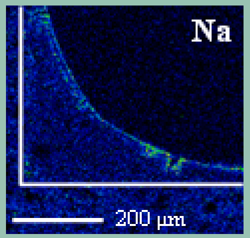
Study fuel- and engine-specific PM to support reduced fuel penalty for emissions control.





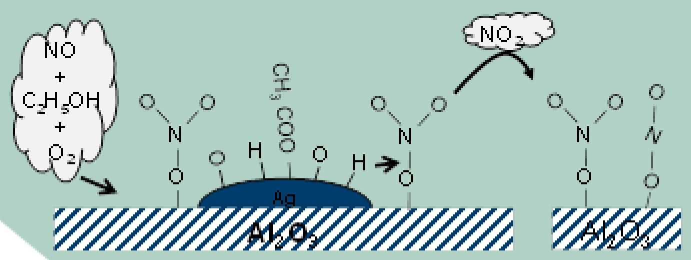
Enable examination of EGR cooler deposits to support models and component development.





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

Identify mechanisms to utilize advantageous fuel characteristics.



New characterization techniques and engagement with industry are key enablers.

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Summary of Technical Accomplishments

- Confirmed that HC-significant deposits that may lead to plugging can result from low-T, low-Re operation, particularly for low-volatility fuels.
- Identified pathway for advantageous use of ethanol in gasoline to enable non-precious metal lean NO_X aftertreatment for high-efficiency lean-burn engines.
- Determined Na affects SCR oxidation sites; launched expanded collaborative effort with Ford, NREL, MECA, and NBB to rapidly asses full-size systems.
- Determined that soot oxidation kinetics depend on fuel properties but also on engine operating conditions.
- Identified fuel-range HCs as the dominant species responsible for de-activation of SCR catalysts through direct analysis of the monolith by pyrolysis GC/MS.

Fuel Effects on EGR Cooler Fouling

Does use of biodiesel blends and other non-traditional fuel formulations worsen cooler fouling compared with ULSD?

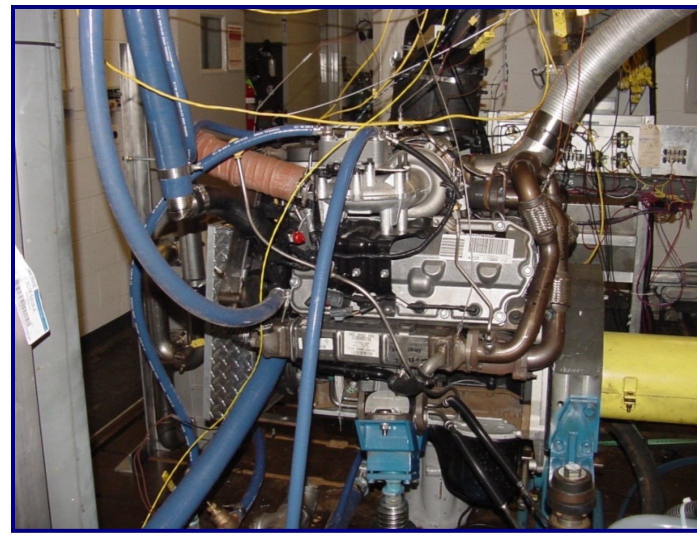
Benefit: Mitigating concerns and potential issues with EGR cooler fouling associated with expanded biodiesel use can enable broader utilization to displace petroleum consumption.

Accomplishments: Demonstrated that HC-significant layers can build up extensively without effectiveness loss, potentially leading to plugging.

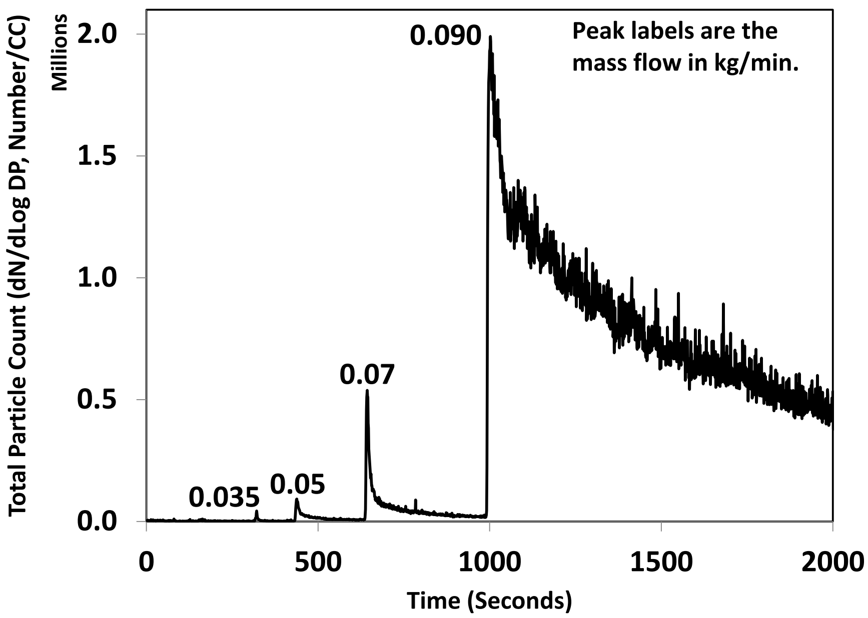
- Showed that extended operation at low-Re, low-T conditions can build significant deposit layers high in fuel-HCs with very little effectiveness loss.
- Found that removal by flow-induced shear is suppressed in HC-rich deposits.
- Determined that spall material is not re-entrained diesel particulate, but rather has different characteristics than typical diesel particles.

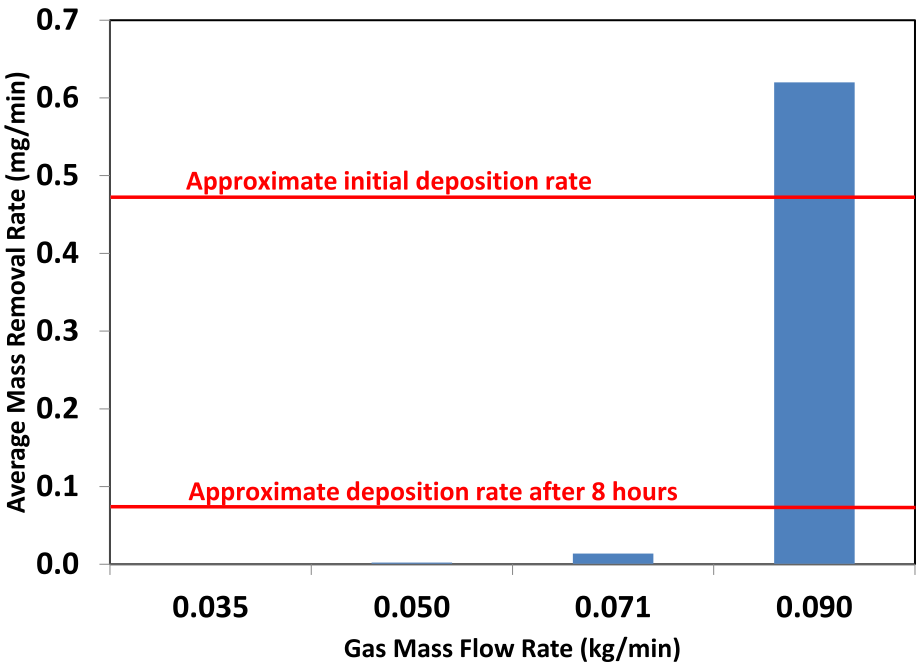
Surrogate EGR cooler tubes are employed to enable multiple analyses of deposits.

- **Ford 6.4-L V-8 used as exhaust generator.**
- **Surrogate tubes provide more accessible samples for study than full-size coolers.**
- **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 and physical properties



One key question in cooler fouling is whether deposits are removed by shear forces; results show this is possible but may not be practical.





Spalling of Particles

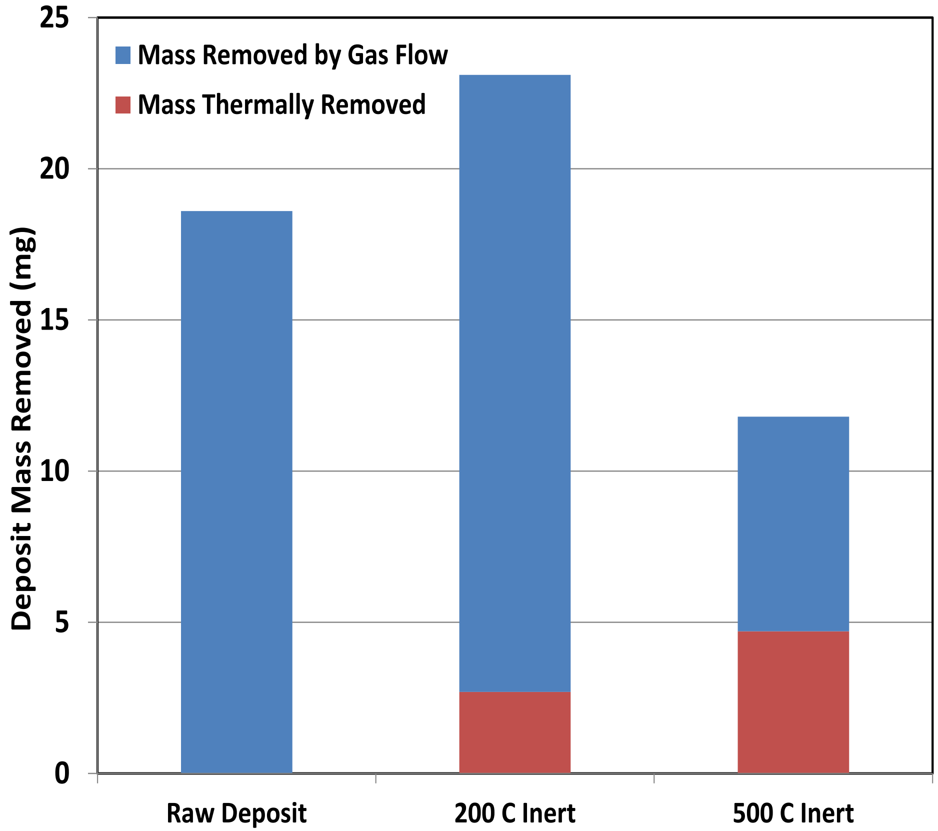
- Significant beginning at 0.071 kg/min/tube or 45 m/s gas velocity.
- Insignificant at flows comparable to or lower than the deposition flow rate. (<15 m/s)
- Removal velocity causes high pressure drop (~1 PSIG); likely not practical.
- Spalls are not simply re-entrained diesel particulate (see supplemental slides).

Practical removal of deposits likely requires processes or geometries that impose an uplift force on the deposit to augment flow-induced shear forces.

Differing removal rates have been observed.

HC-Significant Deposits:
- **Shear-induced removal is suppressed for HC-dominated deposits.**
- **Density (thickness), tensile strength, or both?**

Low-HC Deposits:
- **Raw deposit and 200C case have similar mass removal.**
- **500C case showed much less mass removal.**
  - Sintering of the deposit.
  - Higher resistance to shear.



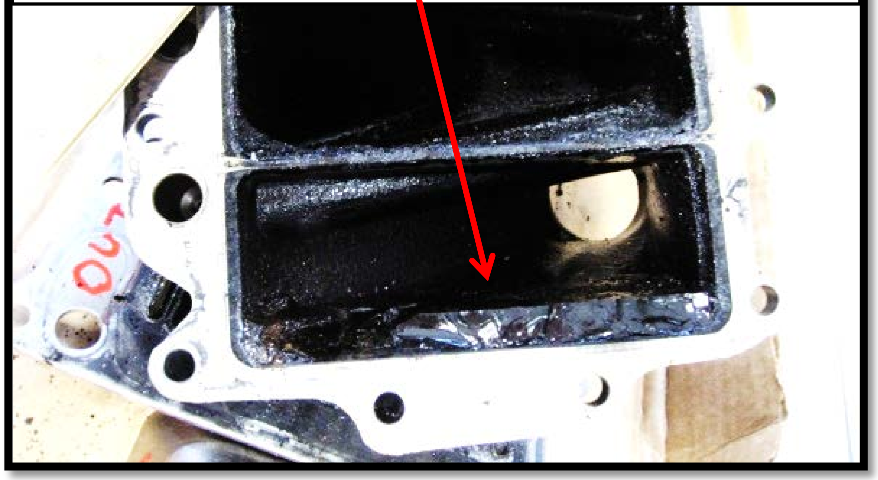
Total deposit mass before removal ~ 60mg.

Deposit thermochemical history (including HC content and chemistry) can significantly influence deposit removal through spallation.

Fuel-related HCs can contribute to fouling through the formation of a relatively dense deposit under low-temperature conditions.

- **Operation at low-T, low-Re conditions develops HC-rich deposits.**
- **Experiments have shown high deposit mass with very little effectiveness loss.**
  - Density must increase significantly.
- **Deposit HC content >50%.**
- **Can continue unabated for long periods.**

Image of a glass-like deposit in an OEM cooler diffuser; ~ 1cm thick and 80% volatile content.



HC deposition is strongly a function of the wall temperature and volatility of the HCs; expanded use of higher-boiling HCs (such as biodiesel) in fuel is expected to increase the risk of plugging.

Fuel Effects – Exploiting Alcohols in Gasoline to Enable Lean NO_X Reduction

Can broad inclusion of bio-derived alcohols in fuel may improve the viability of fuel-efficient lean-burn vehicles by enabling a non-precious metal route to NO_X reduction?

Benefit: Use of lean-burn technology can reduce the tank-mileage penalty associated with high ethanol blend levels and encourage broader utilization. Taking advantage of the properties of ethanol will enable the use of non-precious metal catalyst systems for lean-NO_X reduction.

Accomplishments:

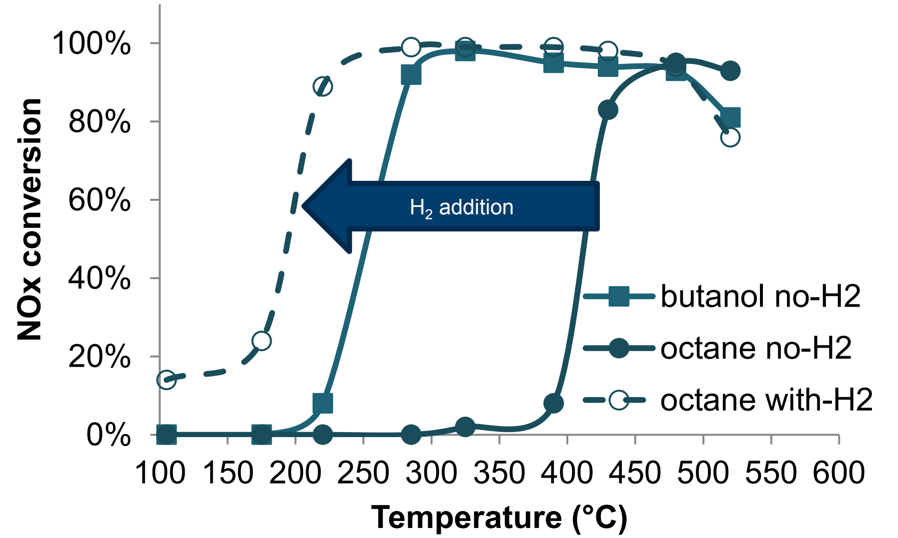
1. Demonstrated high NO_X reduction reactivity with high selectivity to N_2 using ethanol as a reductant over silver-alumina catalyst.

2. Illustrated role of ethanol is similar to HC-SCR activation observed with H_2.

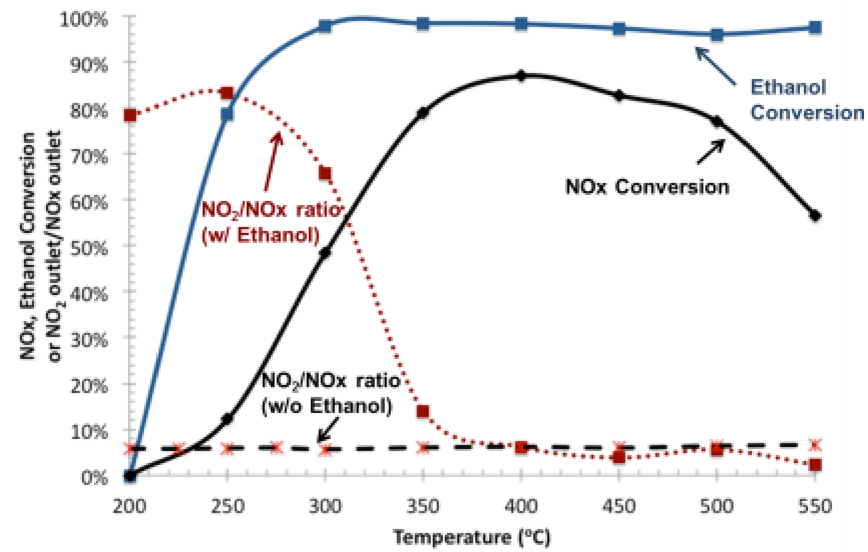
Inclusion of bio-derived alcohols in gasoline creates unique opportunities for PGM-free NO_X reduction catalysts to support lean-burn engines.

- Ethanol/butanol inclusion in gasoline may promote NO_X reduction using octane/higher-HCs.
- NO_X reduction activity using octane is enabled by H_2; similar to ethanol mechanism.
- Ethanol and butanol show low temperature NO_X conversion on silver catalysts.
  - Similar NO_X reactivity to H_2+octane.
  - Suggests similar mechanism.

EISA mandates have resulted in virtually all gasoline containing ethanol; this presents an opportunity to capitalize on the beneficial properties of ethanol/butanol.



From R. Burch, Cat. Rev. Sci. Eng. 46 (2004) 271.



From Toops et al., in press, Catal. Today (2012)

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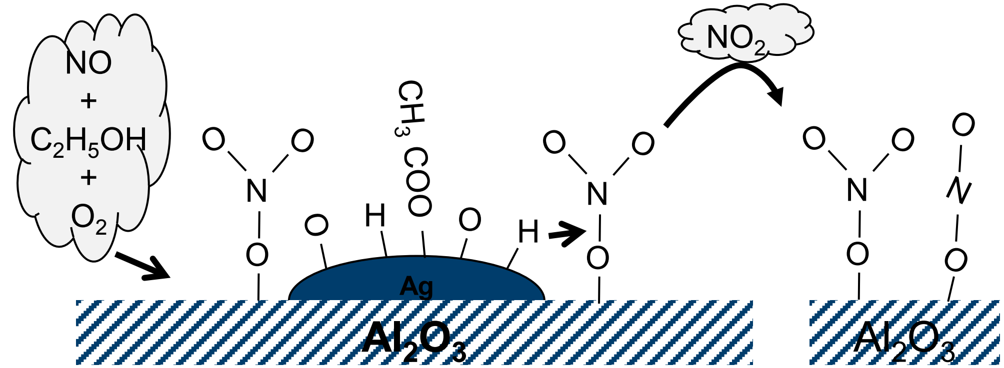
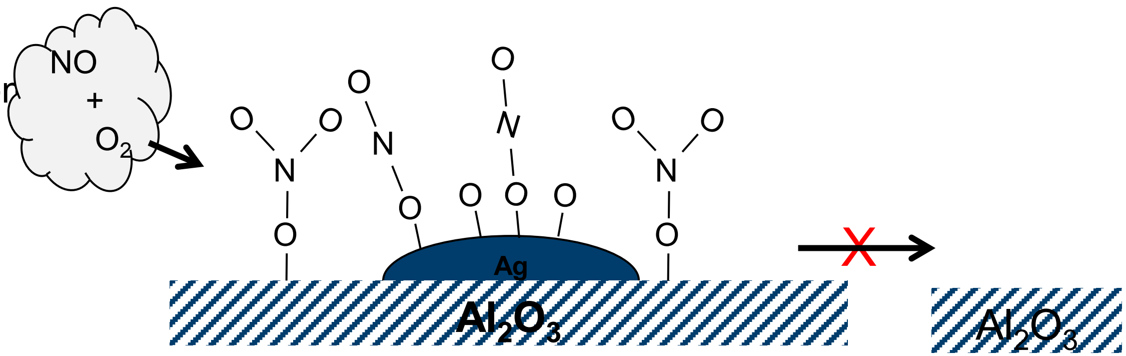
Recent fundamental study determined the beneficial role of ethanol in NOx reduction with silver/alumina catalysts.

- **Ethanol + O_2 readily forms acetates**
  - de-hydrogenation is first step
  - Leads to adsorbed H (H—*)
- **H—* releases nitrates as NO_2**
  - enables adsorption away from Ag;
  - Increases N population on catalyst surface.
  - new reactive/adsorption site becom available
- **Similar to H_2 enhanced HC-SCR**
- **NO+O_2 yields minimal nitrite/nitrate formation**
  - low mobility w/o ethanol
  - Illustrates NO inhibition
  - DRIFTS supported finding





References Consulted:

A.B. Mhadeshawr et al., Appl. Catal. B 89 (2009) 229; S. Chansei et al., J. Catal. 276 (2010) 49; Y.H. Yeom et al., J. Catal. 238 (2006) 100; Shimizu et al., Appl. Catal. B 30 (2001) 151. R. Burch, Cat. Rev. Sci. Eng. 46 (2004) 271.

Hydrogen from dissociative adsorption of ethanol facilitates NO_X reduction over Ag/Al_2O_3; may enable utilization of higher HCs by silver catalysts.

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

Benefit: Insuring that the biodiesel blend levels above 5% in the marketplace does not adversely impact emissions control devices will enable broader utilization of blends such as B20.

Accomplishments:

1. Identified that oxidation functionality is the most impacted characteristic of SCR-performance when exposed to Na equivalent of 450,000 miles of B20.

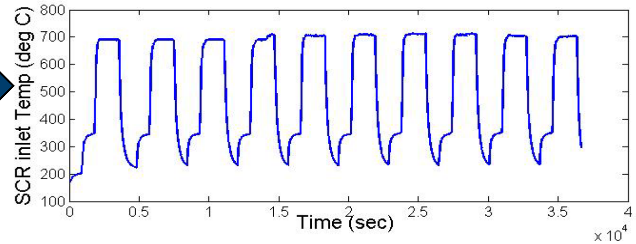
2. Began large collaboration between ORNL, NREL, NBB, MECA, and Ford to perform full-size catalyst study with current commercial emissions control system.

Current 5 ppm Na limit is a concern for emissions control devices, especially for heavy duty applications.

- NaOH or KOH typically used in biodiesel production
  - Liquid-phase catalyst
- Current ASTM specification
  - 5 PPM for total alkali content (Na+K)
  - 5 PPM Calcium + Magnesium
- Primary concerns are its impact on
  - ash accumulation in DPF,
  - mechanical strength of substrates
  - zeolite-based SCR deactivation
- Collaboration with NREL, NBB, MECA, and Ford to perform full-size catalyst study with current commercial emissions control system

Based on initial findings in studies at ORNL/NREL/Ford large collaborative effort undertaken to establish thresholds

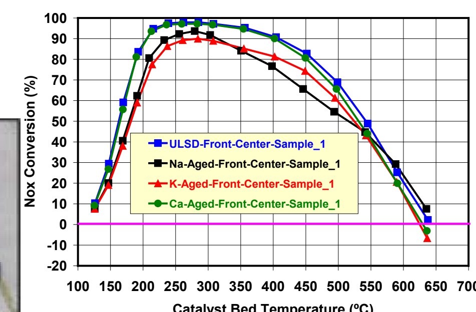
- Collaboration with NREL, NBB, MECA, and Ford focusing on light duty applications
  - full production exhaust systems from 2011 Ford F250; DOC→SCR→DPF



Ongoing study expected to conclude this FY

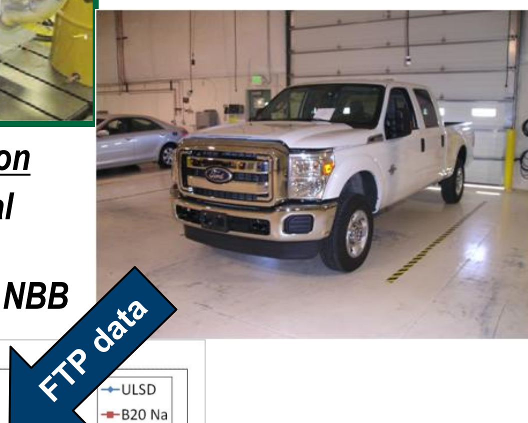
Ford leading catalyst functionality study

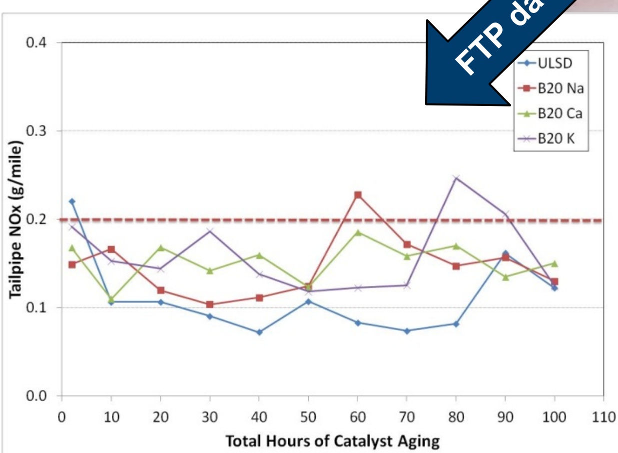
- *Sectioned study of DOC and SCR*
- *Determine what level of Na, Ca, and K leads to decrease in performance*



NREL leading engine operation

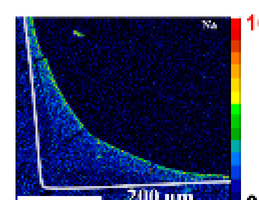
- *Na, K, and Ca plus thermal exposure; ULSD-only too*
- *Coordinating with MECA+NBB*





ORNL leading materials characterization

- *DPF materials characterization*
  - *Co-funded by Propulsion Materials*
- *Identify level of Na, Ca, and K in each section of the emissions control devices*



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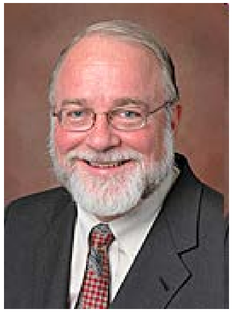
Collaborators and Partners

- Fuel Effects on EGR Cooler Fouling
  - Ford/GM/Modine: experimental guidance
  - ORNL Advanced Manufacturing Center (DOE-AMO)
- Lean NO_X 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
- Fuel Effects on Emissions Control Devices
  - NREL/Ford/MECA: Biodiesel-aged collaborative effort
  - University of Tennessee: graduate research
  - CLEERS: evaluation protocols
- Fuel Effects on PM Oxidation Kinetics
  - Penn State University: microscopy and PM structural analysis, generation of biodiesel PM with medium-duty engine.



Future Directions (Beyond FY12)

- **Fuel Effects on EGR Cooler Fouling:**
  - Future EGR efforts will focus on low-temperature conditions (such as drop-to-idle) where fuel-related HCs can play a significant role in cooler performance and degradation.
- **Exploiting Alcohols in Gasoline to Enable Lean-NO_X Reduction:**
  - Investigate ethanol and butanol ability to improve HC-SCR NOx reduction reactivity with Gasoline blends.
  - Study formation of NH_3 under lean operation (potential for hybrid SCR system)
- **Biodiesel-based Na Impacts on Emissions Control Devices:**
  - Study concluding; will present assessment of 5 PPM limit impact on light-duty engineering margins.
  - Assessing the need to perform similar study with heavy-duty and lubricant communities.

- **Assessment of Properties, Emissions, and Compatibility of Emerging Fuels:**
  - Utilize pyrolysis GC/MS capability to investigate fuel and lubricant contributions to PM formation in GDI and other advanced engines.
- **Soot oxidation kinetics work is concluding in FY12. A follow-on activity investigating GDI PM production and characteristics is being initiated.**

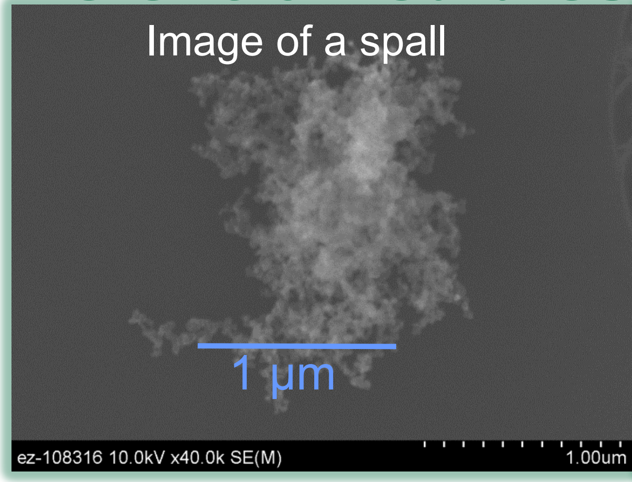
As always, we welcome specific concerns from industry, whether in these areas or other topics, for future studies.

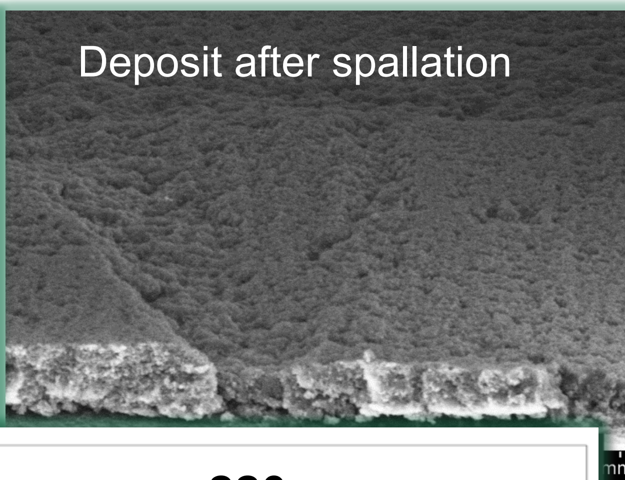
Summary

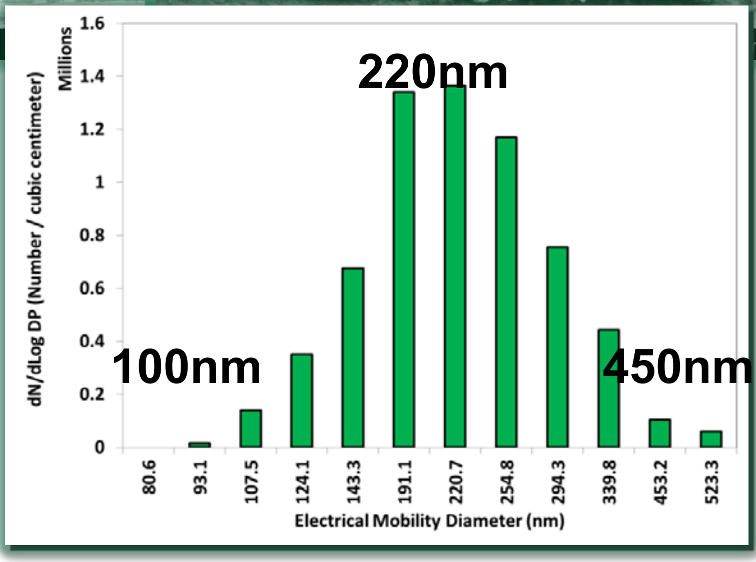
- **Relevance:** This project is targeted towards providing data and predictive tools to address gaps in information needed to enable increased use of NPBFs. (DOE Technical Barrier)
- **Approach:** The approach being pursued is to bring together targeted, engine-based studies using NPBFs with in-depth characterization of PM and HCs to better understand behavior for specific technologies. (Currently emissions control devices and EGR Systems)
- **Collaborations:** Collaborations with several industry stakeholders and universities are being used to maximize the impact of this work.
- **Technical Accomplishments:**
  - Low-Re, Low-T conditions produce HC-significant deposits that may lead to plugging; removal of deposits by flow shear requires very high velocities.
  - Identified pathway for advantageous use of ethanol in gasoline to enable non-precious metal lean NO_X aftertreatment for high-efficiency lean-burn engines.
  - Determined Na affects SCR oxidation sites; launched expanded collaborative effort with Ford, NREL, MECA, and NBB to rapidly asses full-size systems.
  - Determined that soot oxidation kinetics depend on fuel properties but also on engine operating conditions.
- **Future Work:** Plans are in place; industry input towards those plans or other fuel-emissions control effect concerns is needed and welcomed.

TECHNICAL BACKUP SLIDES

Spalls from the EGR cooler deposit are not simply re-entrained diesel particulate.





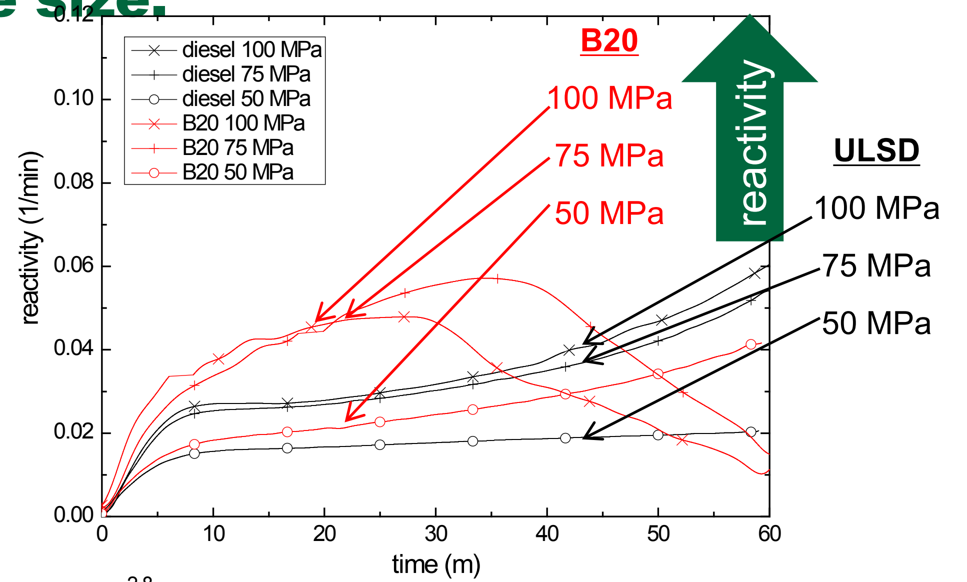


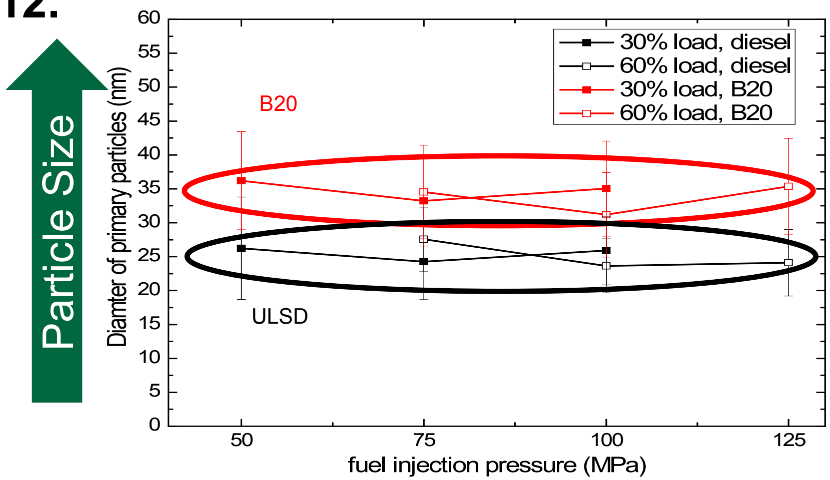
- Spalls are much larger than typical diesel particulates.
- Areas experiencing spallation become rougher than the parent deposit.
- Observations point to the formation of a cohesive deposit even during short time periods.

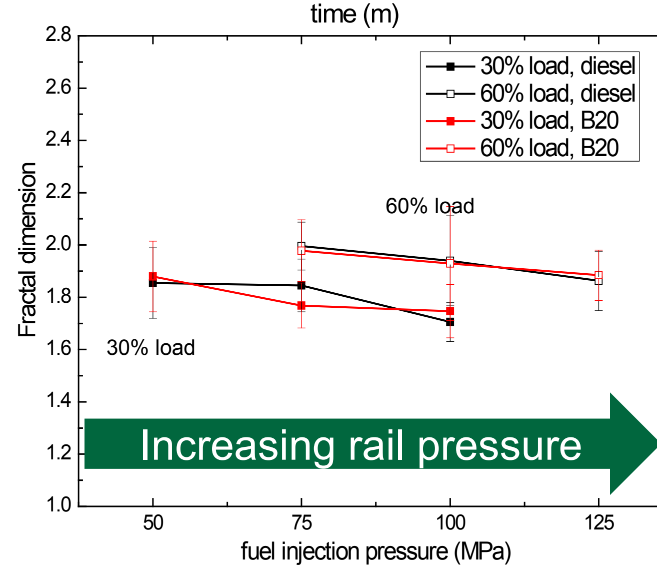
Formation and removal of deposit spalls is complex; critical-velocity models may not adequately capture the underlying physics.

Fuel-type and engine operating conditions affect soot reactivity and primary particle size.

- B20 soot more reactive than ULSD.
- Higher injection pressure increases reactivity.
- B20 soot has higher average primary particle size
- Soot disorder (fractal dimension) increases with higher load.
- Study being brought to completion in FY12.







Engine operating conditions do influence subsequent soot oxidation kinetics.

Summary of key biodiesel PM oxidation findings

- **Rate of O_2-based oxidation of the fixed carbon component of diesel PM is directly dependent on available surface area.**
  - Surface area evolves differently with burnout based on fuel type.
  - A single Arrhenius rate expression with E_A = 113±6 kJ/mol can be used to fit surface normalized rates for all fuels studied.
- **O_2-based oxidation rates of nascent PM can be modeled as the sum of a volatiles evolution term and an Arrhenius FC consumption term.**
- **NO_2-based oxidation of diesel PM by appears to be very different from oxidation by O_2 and shows little fuel dependence.**
- **DPF models need to account for biodiesel blending, prior oxidation history and O_2/NO_2 concentrations for predicting regeneration rate.**
- **In addition to biodiesel level, increasing injection pressure increases soot reactivity.**

Recommendations for Future Work in PM Oxidation Kinetics

- Continue resolving appropriate kinetics for NO_2 PM oxidation and role of surface area.
- Identify how the combined kinetics for O_2 and NO_2 should be modeled.
- Resolve the appropriate functional form to use for the PM devolatilization rate in the presence of oxidants.
- Expand the range of biofuels and engines evaluated.
- Incorporate the combined O_2/NO_2/devolatilization kinetics models into an integrated DPF device model suitable for vehicle simulations.