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

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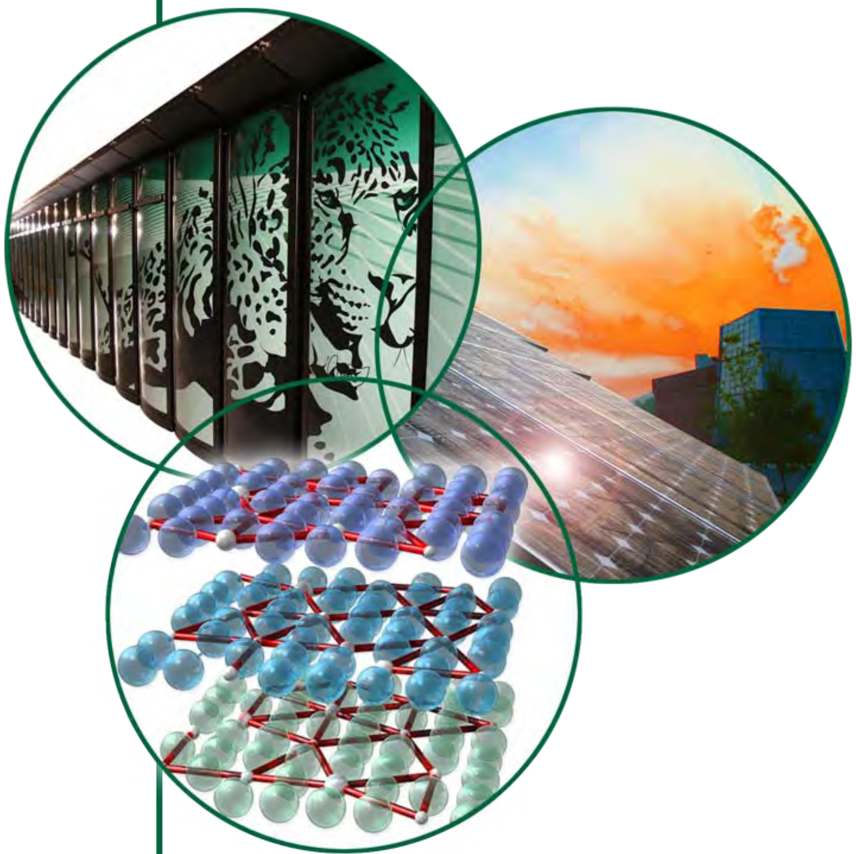
Project ID # FT007



2011 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 property effects on:**
  - combustion and engine optimization
  - emission control system impacts.

Budget

- **Funding received in**
  - FY10: $1100K
  - FY11: $725K
- **Anticipate similar funding level for FY12.**

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

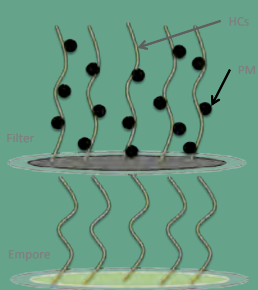
Greater utilization of NPBFs is enabled through understanding and resolving risks associated with their interaction with other components and technologies.

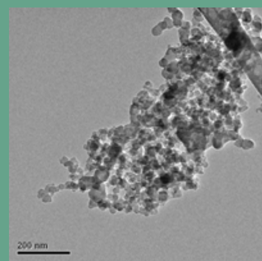
Project Goals: Provide data in support of predictive tools that can be used to understand fuel-property impacts on combustion and emissions control systems.

- **Emerging fuel sources are often not fully understood and may have unintended impacts.**
- **Current vehicles are sophisticated and can be sensitive to fuel formulations.**
- **Accepting new fuels poses regulatory and consumer confidence risks to industry associated with unanticipated failures of vehicles.**
- **Research is aimed at determining effects of new NPBF formulations.**
  - **Compare to standard fuel formulations**
    - **Biodiesel vs. ULSD**
    - **Ethanol vs. gasoline**

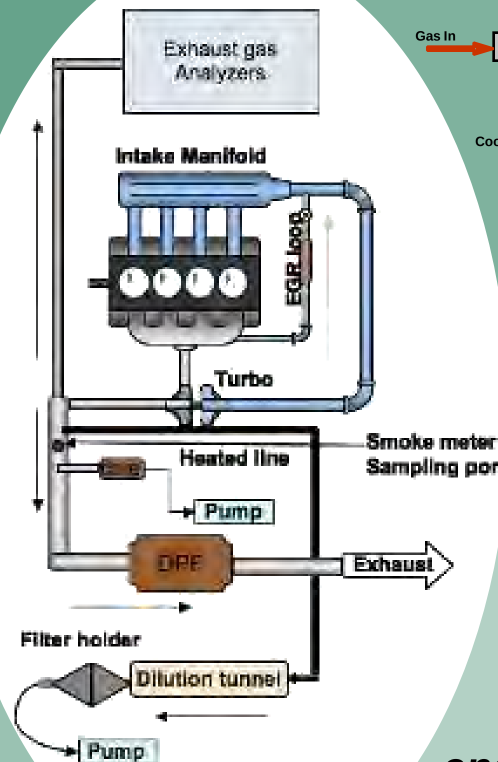
Approach

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.

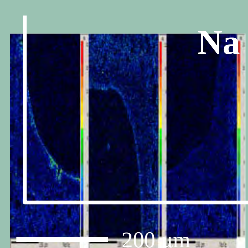




Study fuel- and engine-specific PM to support reduced fuel penalty for emissions control.



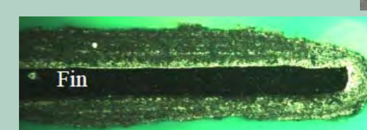
Enable examination of EGR cooler deposits to support models and component development.



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 2011

- **Establish EGR cooler performance and degradation metrics. ($100K)**
  - **Complete study on tube surface treatments.**
  - **Begin studies of HC effects at low-temperature conditions.**
- **Investigate uncatalyzed NO_2 reactivity for NPBF-generated soot in a microreactor study. ($150K)**
- **Establish analytical methods to support NPBF research. ($250K)**
  - **Develop analytical method for analyzing acidic condensates related to use of biofuels.**
  - **Develop method for analysis of urea-related species in deposits and exhaust PM.**
- **Determine sodium impact on DOC-DPF-SCR system. ($125K)**
- **Determine key reactions for NO_X reduction over silver-alumina catalyst. ($100K)**

Summary of Technical Accomplishments

- **Showed that tube surface treatments are not effective at reducing fouling.**
- **Identified conditions for near-term study where HCs may play a role in deposit growth and EGR cooler thermal performance.**
- **Initiated microreactor studies of PM reactivity with NO_2.**
- **Confirmed role of surface area in oxidation rate of devolatilized PM from B5 and B20 fuel blends is consistent with those from B100 and ULSD.**
- **Completed development of exhaust condensate analysis method.**
- **Urea-byproduct method refinement under way.**
- **Showed that sodium from biodiesel significantly degrades SCR catalysts, but placing the DPF upstream can protect the SCR catalyst.**
- **Determined activation energy for NO_X reduction using ethanol over silver-alumina catalyst and demonstrated high reactivity with excellent selectivity to N_2.**

NPBF Effects on EGR Cooler Fouling

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

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

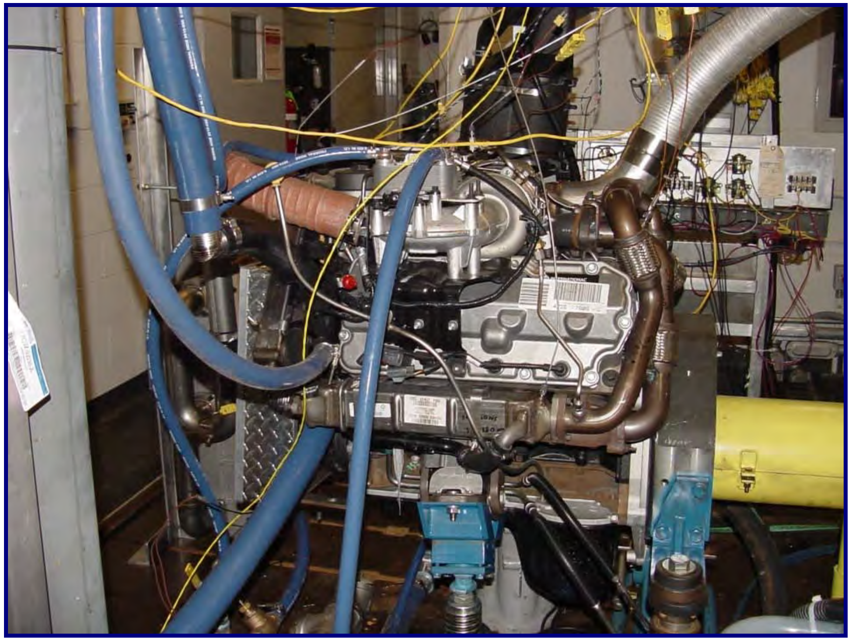
- **Reduces aftertreatment cost**
- **Improves engine system efficiency**

Accomplishments: Completed surface treatment study, examined deposition under controlled transient flows, and formulated a proposed non-dimensional temperature-dependent trapping coefficient.

- **Results to date suggest HCs are only present in significant amounts in cold-wall conditions.**
- **Identified potential conditions where HC (and fuel) effects may become significant.**
- **Showed that during deposit-building, shear-force removal of particles is insignificant at the conditions studied.**

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**



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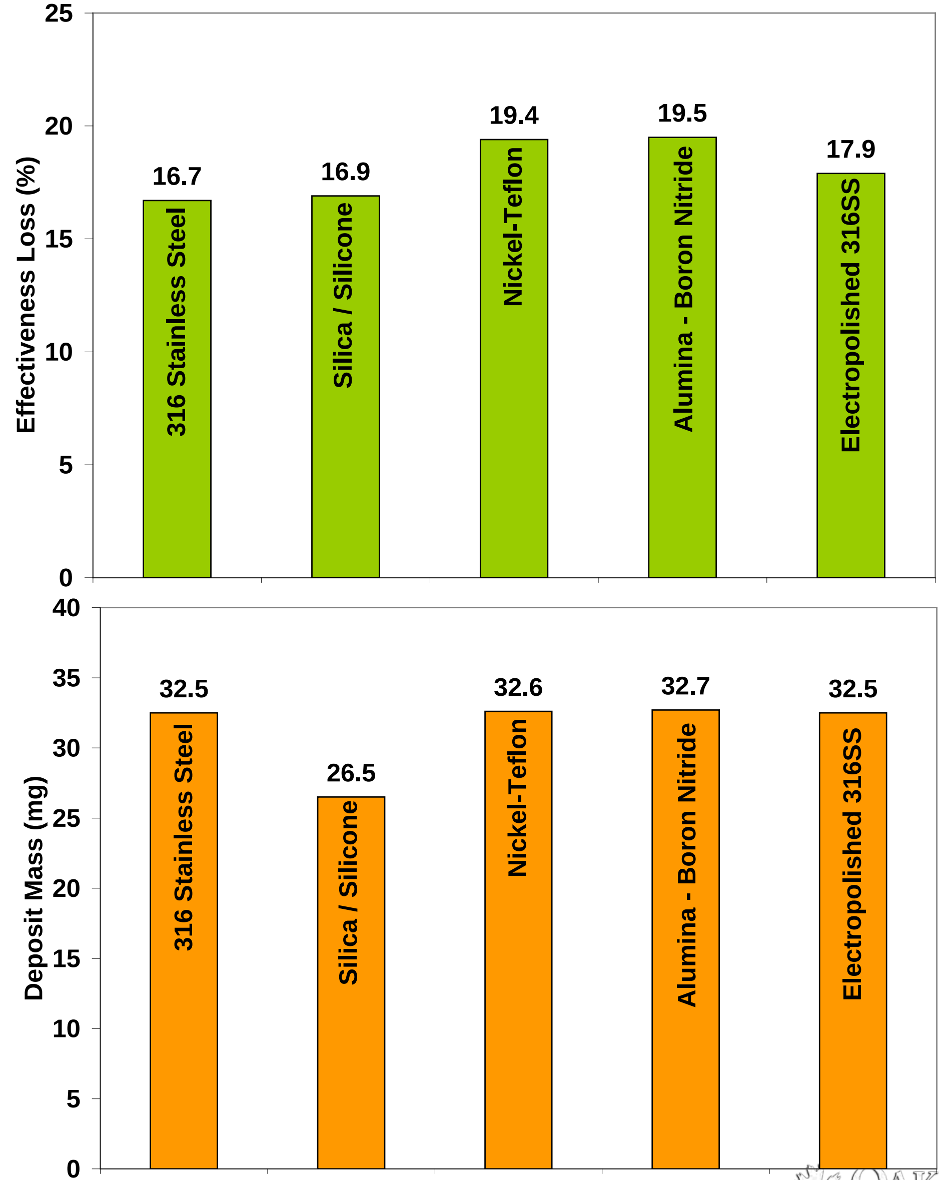
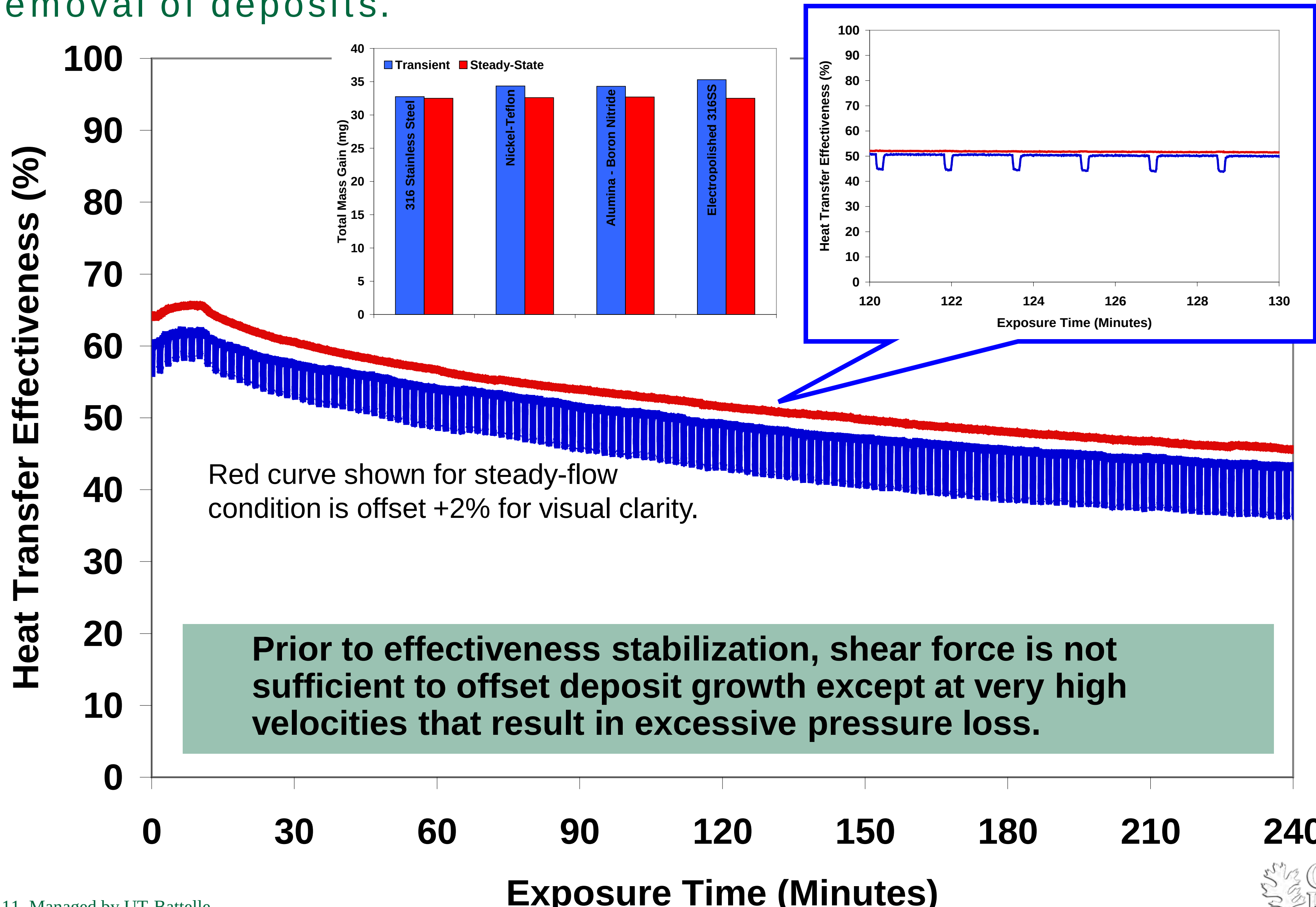
Tube surface treatments have little, if any, affect on deposit growth.

- Ford collaborated to identify and analyze candidate treatments.
- Commercial suppliers coated tube specimens.
  - Slurry or vapor deposition.
  - Stainless steel baseline.
- Some treatments electrically insulating, some conductive.
- Deposit masses and resulting losses in effectiveness very similar.
  - Lower deposit mass for silica/silicone appears to be a result of coating damage during the experiment.
- Previous work with Silcosteel-AC™ showed a small, statistically significant reduction in deposited HCs but no impact on soot deposition.

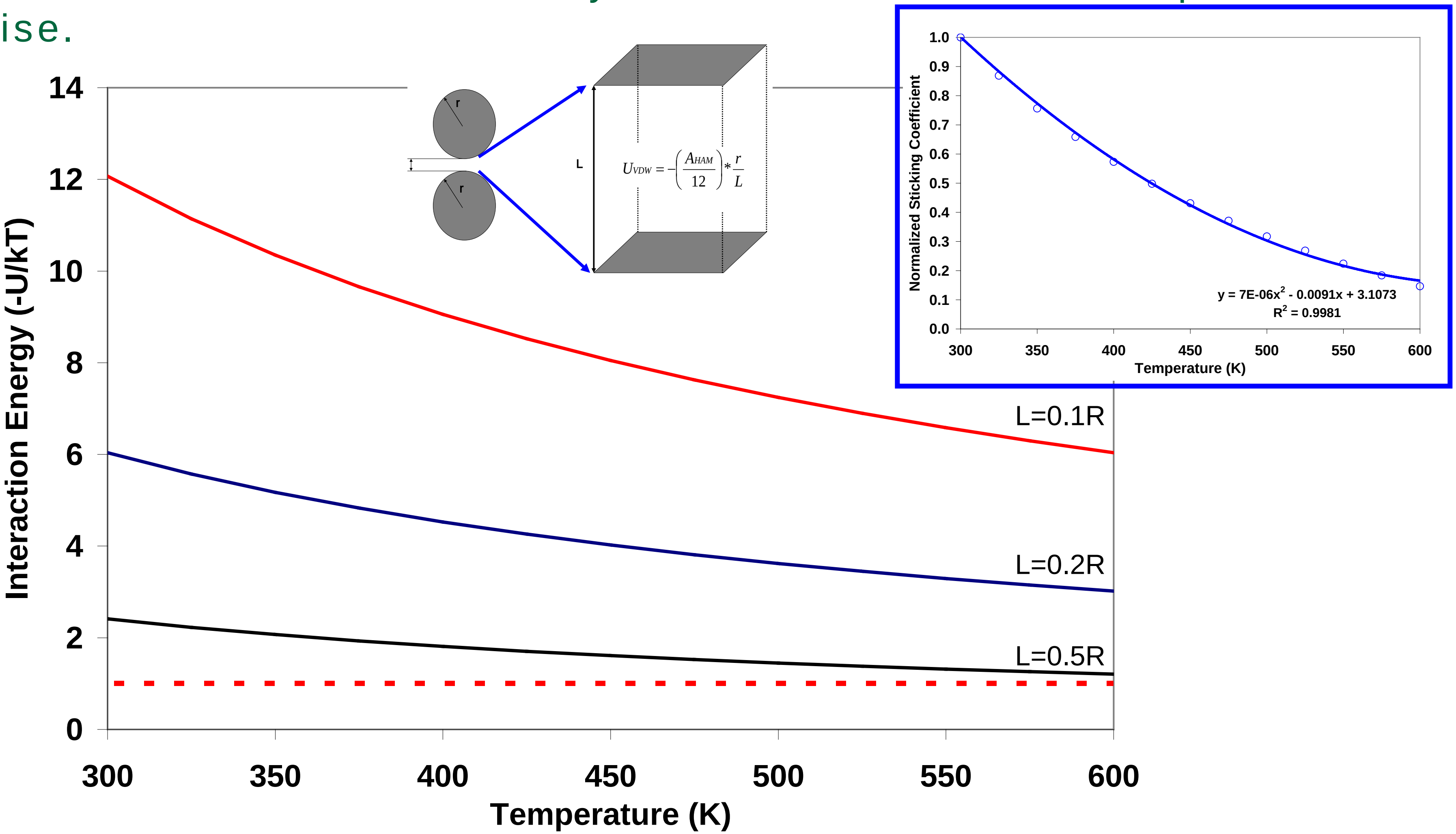
Interrupting deposit binding forces (Van der Waal's forces) through surface modification is not effective at preventing deposit growth.



Doubling the gas velocity periodically to increase shear forces at deposit interface resulted in increased deposition, rather than removal of deposits.

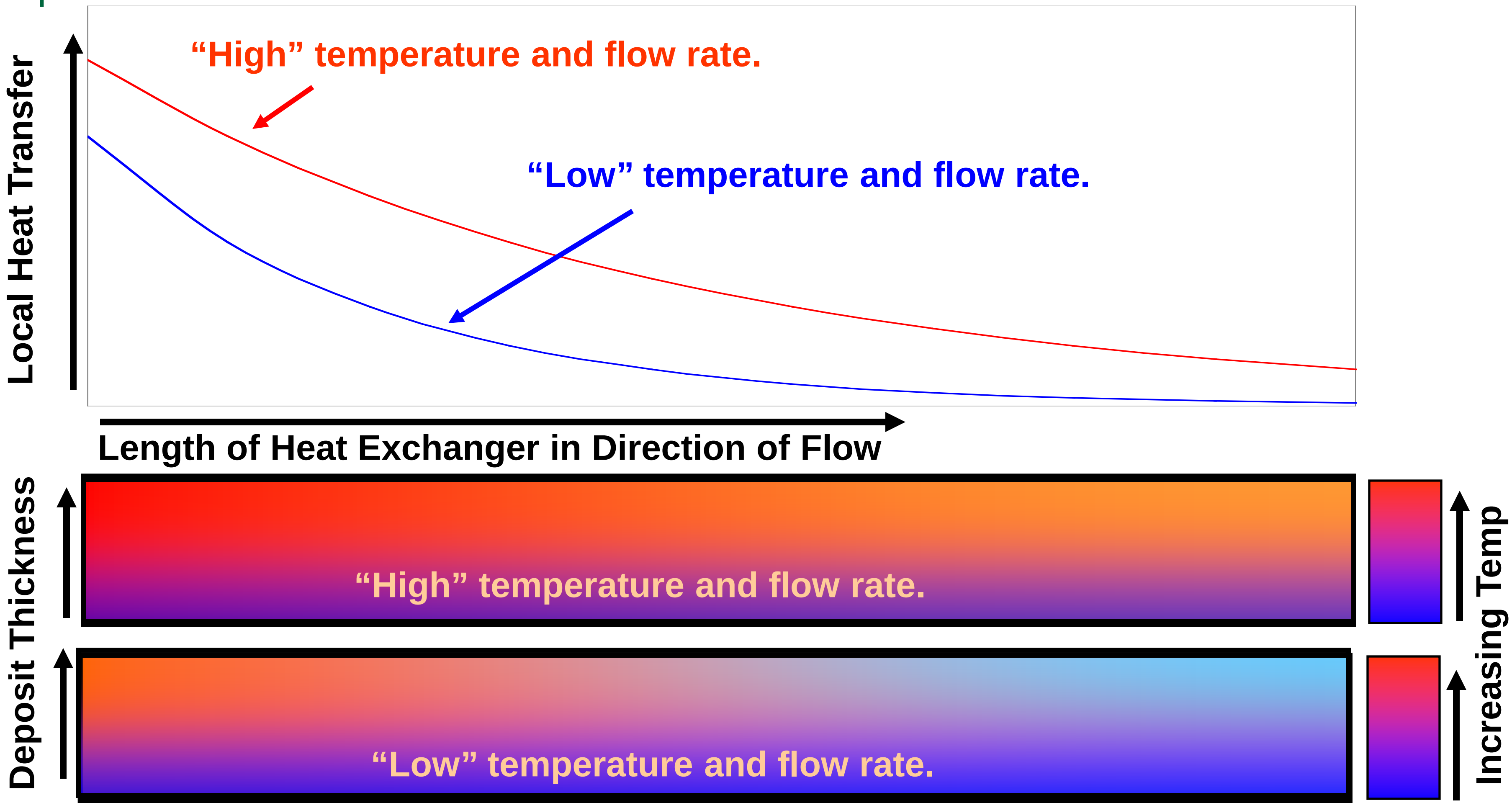


Deposit agglomeration is thought to be a result of Van der Waals forces, which is countered by thermal excitation as temperatures rise.



Reductions in thermophoretic and Van der Waals forces that occur simultaneously due to rising temperatures appear to contribute to the tendency for coolers to achieve a "stable" fouling state.

Deposit layer temperature, and hence HC deposition potential, is dependent on local heat transfer.



Use of a “large” heat exchanger at “low” heat transfer conditions can result in deposit layer temperatures conducive to HC deposition.

Conditions such as drop-to-idle or cold start may result in thermally and physically significant deposit HC levels and may be impacted by fuel chemistry.

NPBF Effects on Particulate Matter (PM) Oxidation

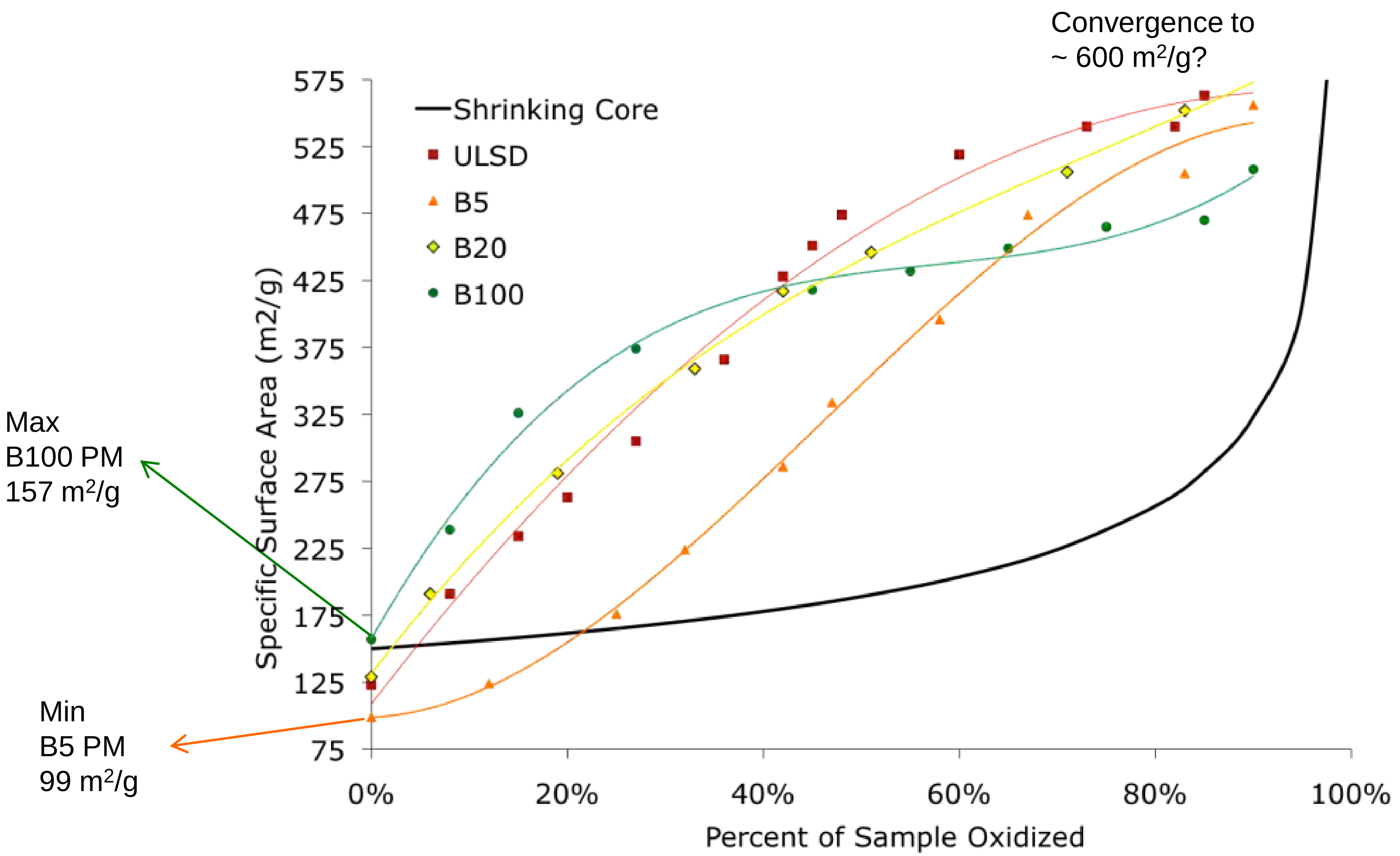
Why does PM generated from biodiesel blends behave differently from that generated from ULSD during DPF regeneration?

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

Accomplishments:

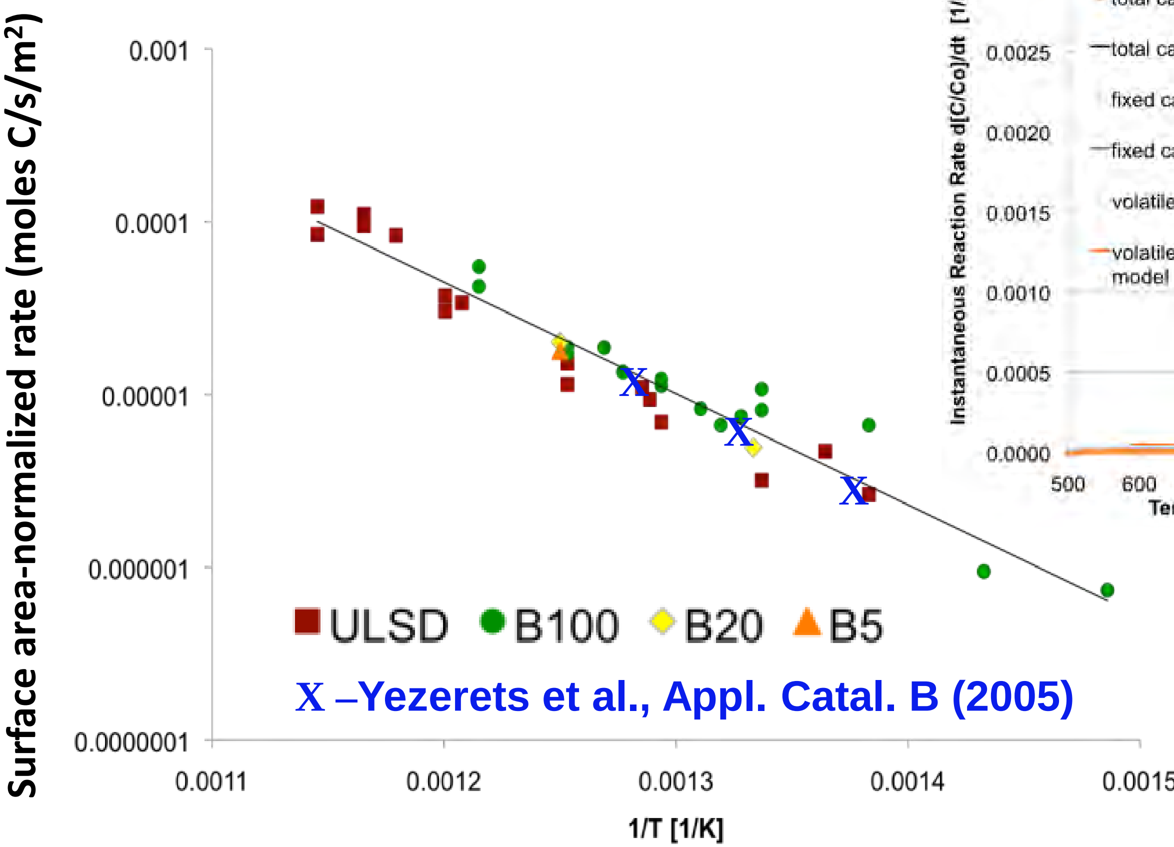
1. **Confirmed surface area role in fixed carbon O_2 reactivity of B5 and B20 PM.**
2. **Observed that biodiesel PM reactivity advantage over ULSD less for NO_2 than for O_2.**
3. **Expanded collaboration with PSU to include HD diesel PM generation.**
   - **Focus on NO_2 reactivity**
   - **Samples from 6 different operating points (3 rail pressures, 2 loads) on Ford 6.7L Powerstroke.**
   - **Evaluating soy biodiesel blends vs. ULSD.**
   - **PSU analyses include BET, TGA, TEM for O_2 and NO_2.**
   - **Micro-reactor characterizations at ORNL include TPO, TPD, isothermal O_2/NO_2 kinetics, BET.**

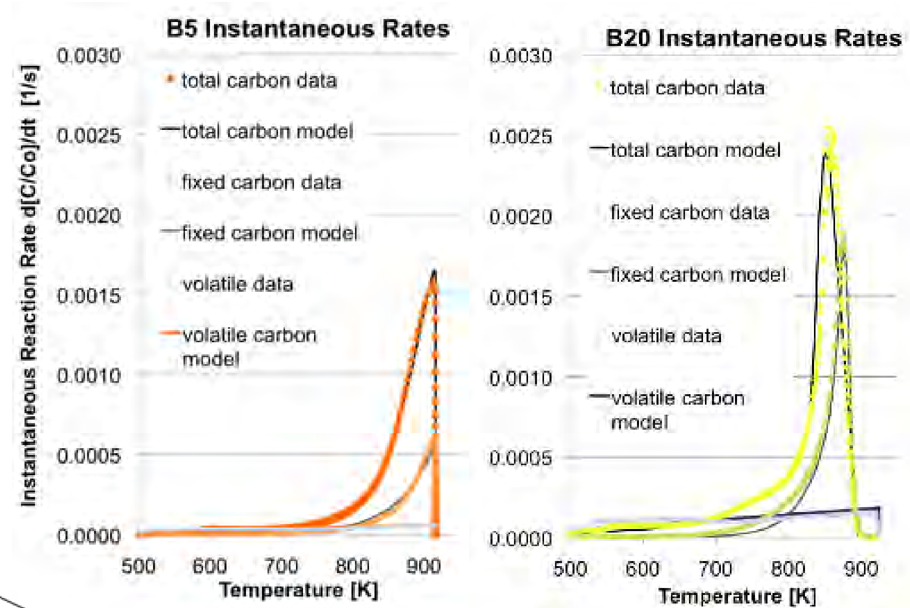
Surface area trajectory during burnout is dependent on biodiesel blend level.



Regardless of fuel blend, PM oxidation in O_2 does not follow shrinking core profile, which suggests evolution of a complex surface.

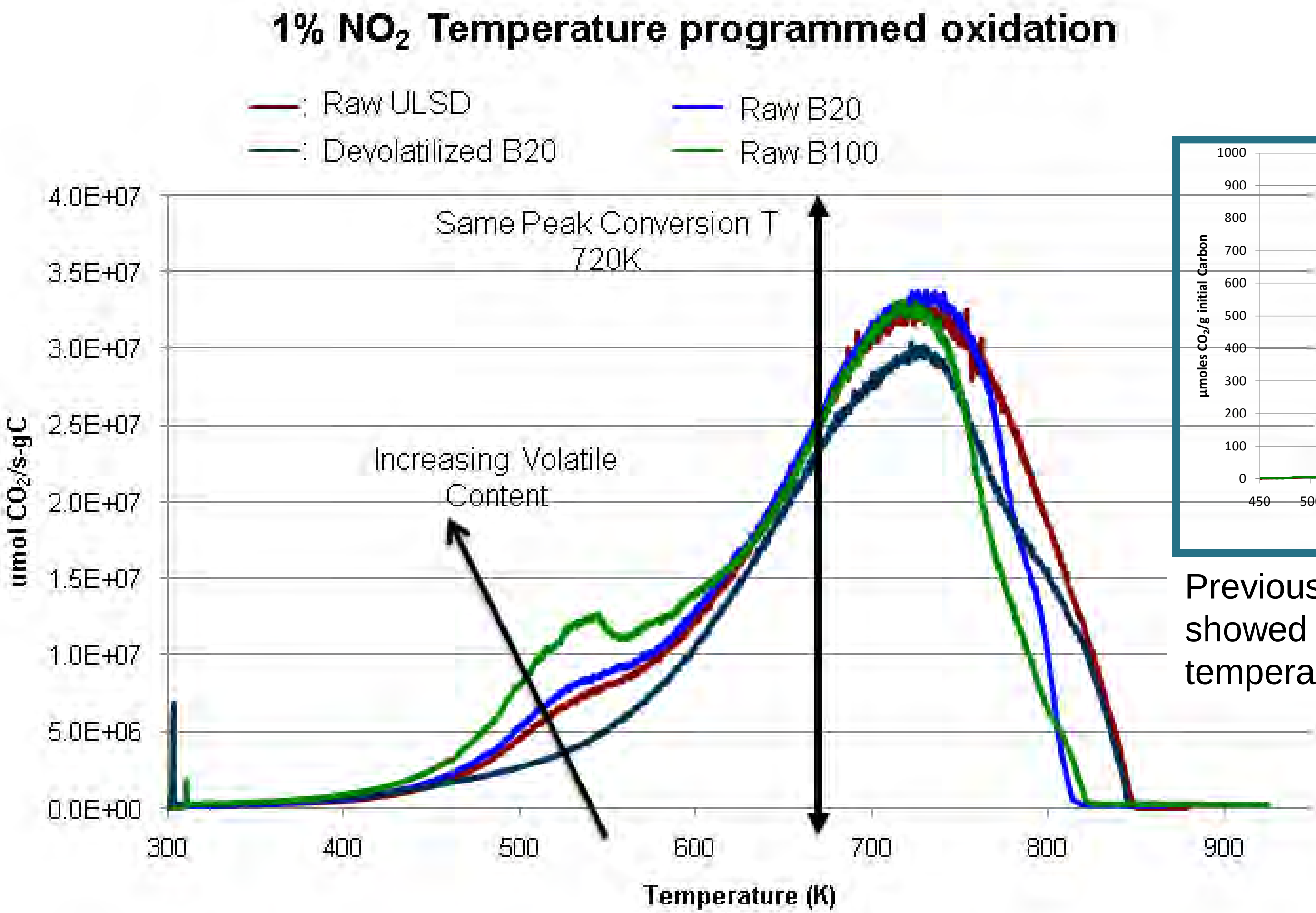
Normalizing oxidation rate to the active surface area eliminates differences between fuels; models agree well with experimental data.

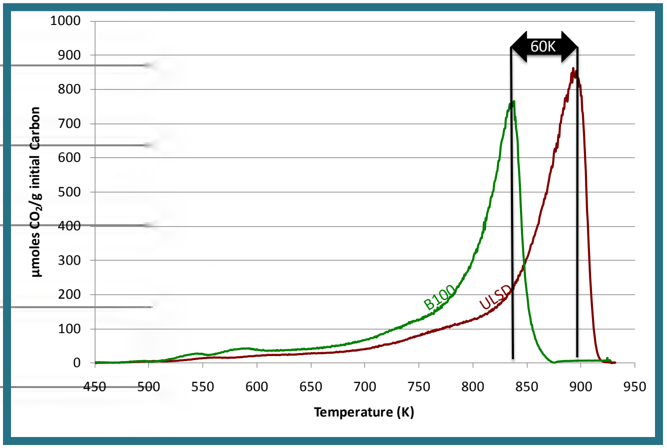




Similar results for Cummins ISB diesel ULSD PM reported by Yezerets et al suggests this surface-area dependent mechanism may be a general pattern for PM oxidation by O_2.

The oxidation rates of B100, B20, and ULSD PM appear to be much more similar in NO_2 compared to O_2.





Previous experience with O_2 (above) showed difference in peak conversion temperature for biodiesel blends.

The collapse of fuel-related differences for oxidation by NO_2 (without normalization to surface area) implies a mechanistic difference for this oxidation pathway.

NPBF Effects –
Biodiesel-based sodium effects on emissions control

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

Benefit: **Identify effects 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:

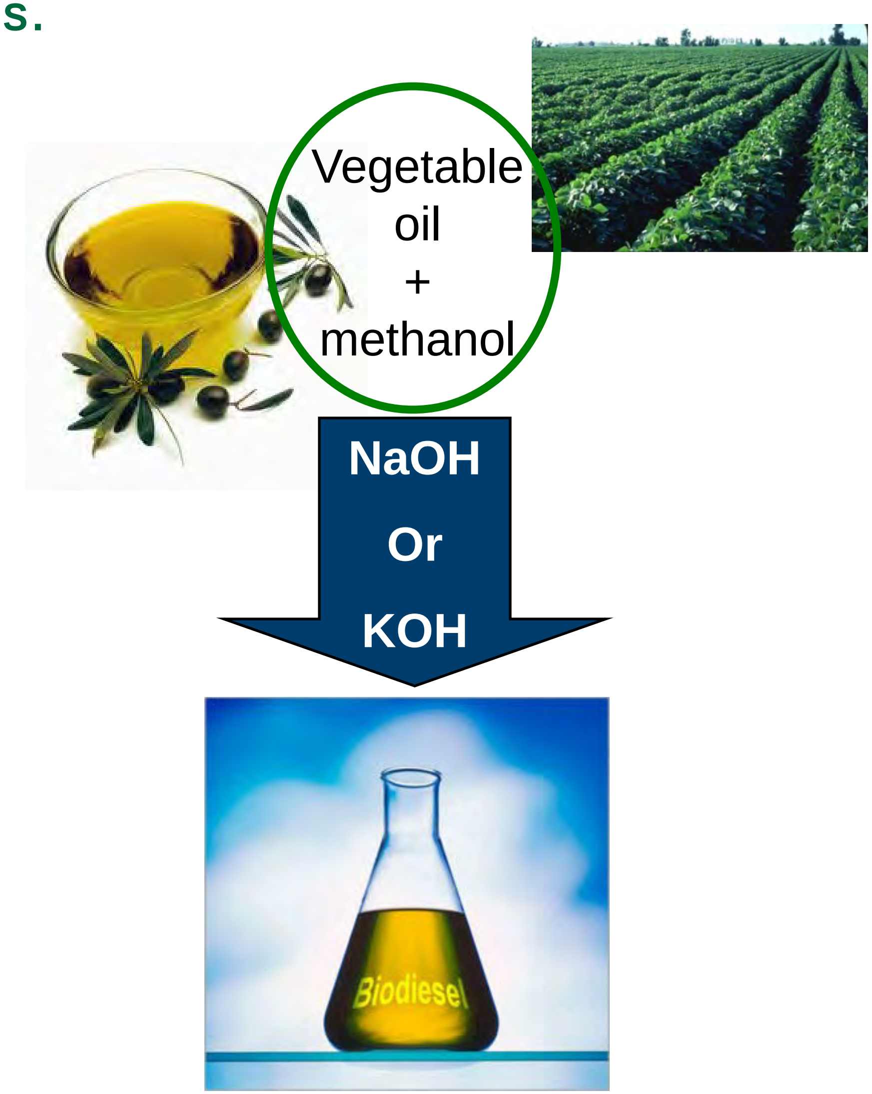
1. Materials characterization of DPF illustrates Na-ash will accumulate in DPF, but levels are substantially less than oil-based ash accumulation.

2. Identified the oxidation functionality of SCR is impacted by Na addition in accelerated Na-addition for 435,000 mile case.

3. Determined DPF protects SCR catalyst from Na when DOC→DPF→SCR orientation is employed.

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 for Biodiesel is 5 ppm for total alkali content (Na+K)**
- **Primary concerns are its impact on**
  - **ash accumulation in DPF, and**
  - **zeolite-based SCR deactivation**
- **Project employs accelerated approach to identify potential problem areas**
- **Efforts reported last year showed no impact on LNT or DOC**

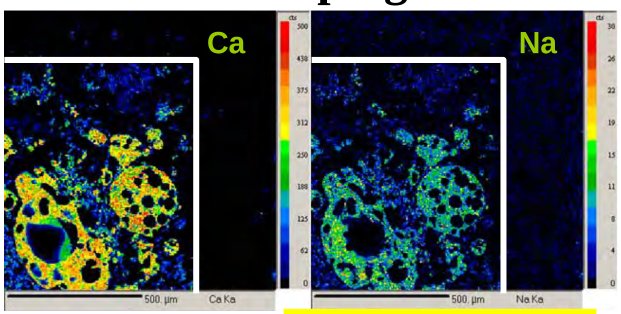


Na-based ash observed in both field- and accelerated-aged DPFs, but at levels much lower than lube oil-based ash.

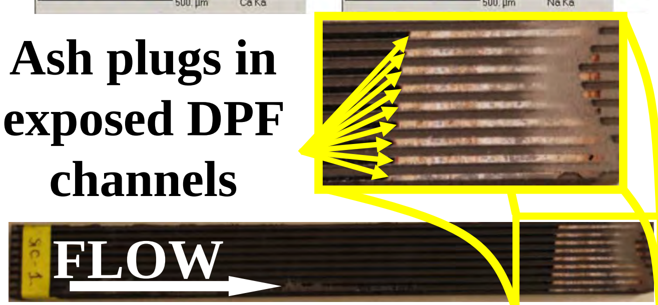
Field-aged sample:

- ***DPF operated for 120,000 miles with B20 that was within specification.***
  - DOC → DPF
- ***Ca:Na ratio in Ash is 20:1***

EPMA of ash plugs in DPF

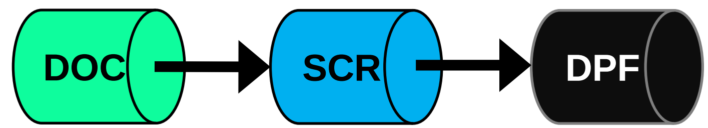


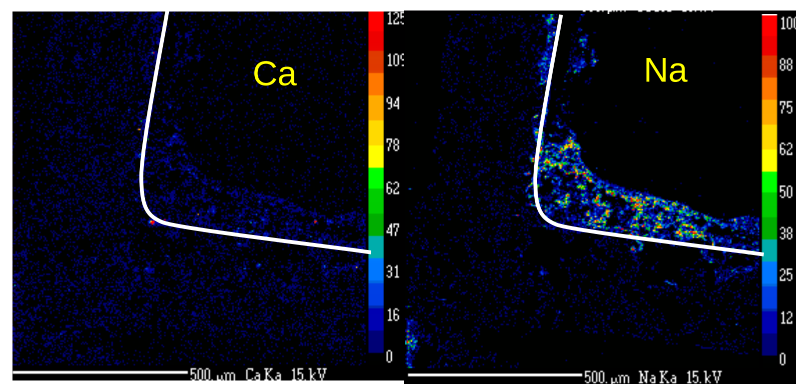
Ash plugs in exposed DPF channels



Accelerated Na-aged sample:

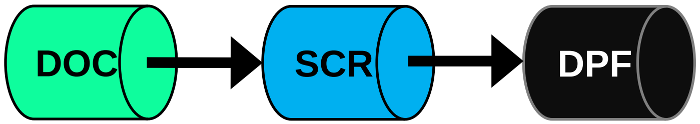
- **435k mile equivalent Na addition**
- **Fuel run in single cylinder Hatz**
- **All ash observed associated with Na**
- **Only small layer observed in appropriately sized DPF**
  - **no Na in cordierite walls**
  - **moderate DPF regen, T < 700ºC**

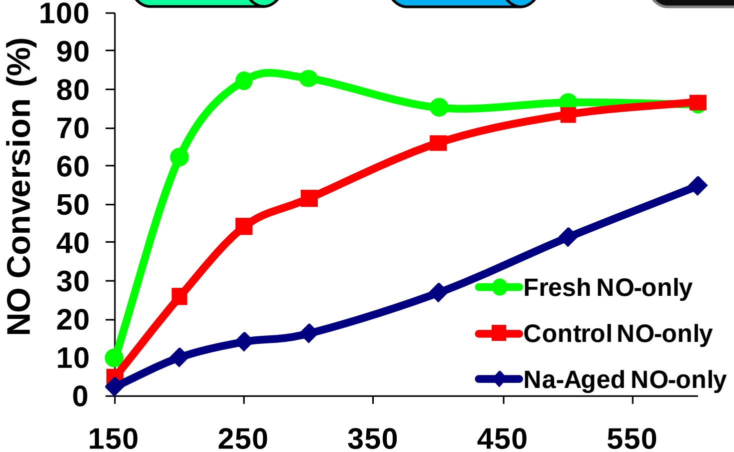


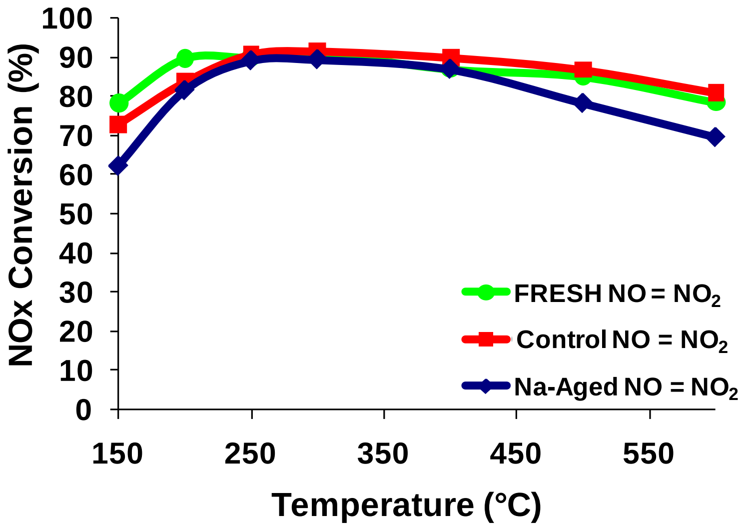


To date, the results obtained with DPFs do not indicate a durability concern from in-spec biodiesel associated with sodium content.

When operating in DOC→SCR→DPF arrangement, significant impact observed on NO reduction rate in SCR catalyst.



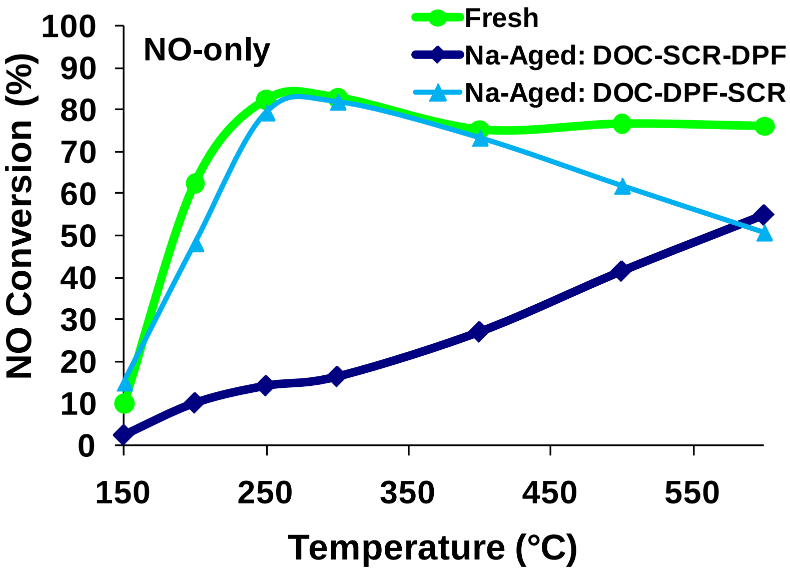


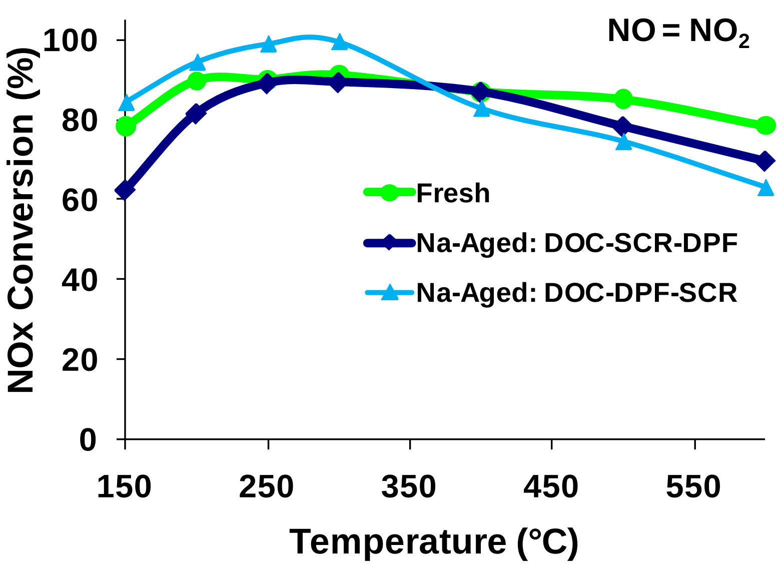


- **Accelerated Na addition using high levels of Na in fuel; 435k mile equivalent Na addition**
  - Engine operated with DPF regenerations
  - First generation zeolite-SCR catalysts
- **When feeding only NO, SCR functionality severely deactivated**
  - Some thermal effects (control)
  - Significant Na effect
- **When NO=NO_2, impact is minimal**
  - NO to NO_2 oxidation limits reactivity
- **0.2 – 0.6 wt% Na observed throughout washcoat**

SCRs can be significantly degraded by even the 5 PPM Na content in biodiesel over the life of the vehicle.

When DPF is in front of SCR, catalyst is protected from Na and its deactivating effects.





- **Below 400ºC, there is no significant effect from accelerated Na-aging if DPF is in front of SCR.**
  - EPMA confirms insignificant Na content in the SCR washcoat.
- **DPF was regenerated at 700C.**
  - SCR protected from DOC exotherm
- **Future considerations will look at higher regeneration temperatures for:**
  - Na migration into DPF wall
  - Na volatization and deposition on SCR

Placing the SCR downstream of the DPF can protect the SCR from deterioration due to Na.

Collaborators and Partners

- **NPBF Effects on EGR Cooler Fouling**
  - **Ford/GM/Modine: experimental guidance**
- **NPBF Effects on PM Oxidation Kinetics**
  - **Penn State University: microscopy and PM structural analysis, generation of biodiesel PM with medium-duty engine.**
- **NPBF Effects on Emissions Control Devices**
  - **NREL/GM/MECA: Biodiesel-aged emissions control devices**
  - **University of Tennessee: graduate research**
  - **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 FY11)

- **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.
- **Soot oxidation kinetics work will continue to be expanded to explore oxidation kinetics with NO_2**
  - Continue collaboration with Penn State University; sponsor graduate research that will be performed at both PSU and ORNL
- **Analytical development:**
  - Research will continue to improve methods for analysis of soot polycarboxylic acids and other key polar species in exhaust and exhaust PM.
- **Biodiesel Sodium+Potassium:**
  - Analyze catalyst cores that have experienced B20 for up to 200K miles.
  - Investigate effects of higher regeneration temperatures in DPF on Na penetration.
  - Continue collaborations to determine acceptable Na+K limit for DOC-SCR-DPF configuration.
- **Ethanol Lean-NO_X Catalysis:**
  - Continue kinetic study with focus on model development
  - Study intermediate formation with emphasis on NH_3
- **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: with several industry stakeholders and universities are being used to maximize the impact of this work.**
- **Technical Accomplishments:**
  - **Surface treatments shown to be ineffective in reducing fouling; conditions where fuel effects may be signficant have been identified for study.**
  - **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; SCR can be protected by upstream DPF.**
  - **Showed that enhanced oxidation of NO to NO_2 on silver-alumina catalyst is key to activating ethanol as a reductant.**
- **Future Work: plans are in place; industry input towards those plans or other NPBF-emissions control effect concerns is needed and welcomed.**