# Fuel and Lubricant Effects on Emissions Control Technologies

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**Oak Ridge National Laboratory**

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**Project ID # FT07**
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**DOE Management Team:**
**Steve Goguen and Kevin Stork**
**Vehicle Technologies Office**

# Project Overview

## Timeline

- Project is ongoing but re-focused each year to address current DOE and industry needs
  - FY13 start: Lubricant Additive
  - FY12 start: Fuel & Lubes GDI PM
  - FY10 start: Lean-Ethanol NOx-SCR
  - FY09 start: Biodiesel-based Na

## Partners

- Industry Collaborators
  - Butamax, Shell, GM, Ford, Cummins, MECA, CDTi, NBB, Umicore
- National Laboratories
  - NREL, PNNL
- Academic
  - Univ. of Tennessee, Chalmers Univ.

## Budget

- Funding received in
  - FY14: $825K
  - FY15: $650K
- Covers 5 sub-projects

## 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)

# Objectives and Relevance


**Objective**

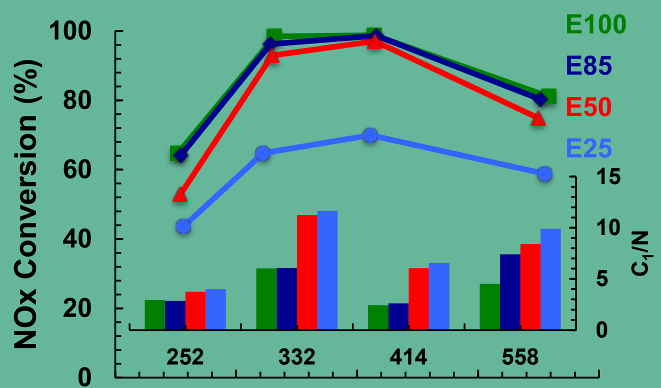
- Provide data to elucidate fuel-property impacts on emissions and emissions control systems
- Identify or alleviate concerns associated with changes in fuels and new lubricants
  - including renewable fuels (alcohols and FAME are current primary focus)
- Investigate unique characteristics of fuels that enable increased efficiency
  - For example, renewable super premium

**Relevance:**

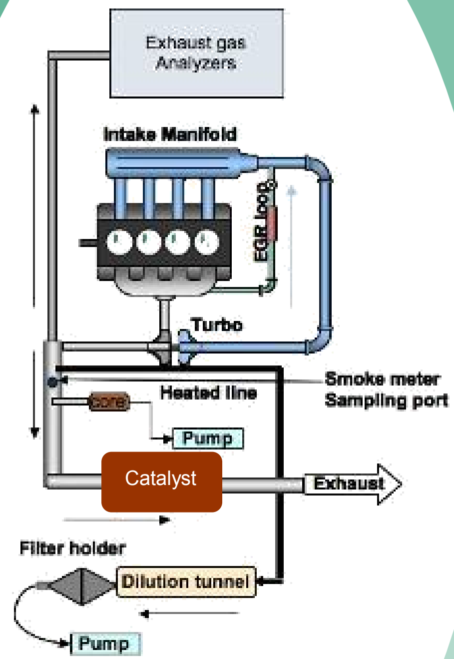
- Addresses Fuels Technology barriers D and E:
  - Inadequate data for fuel effects on emissions and emission control system
  - Inadequate data on long-term impacts of fuel and lubricants on emission control systems.
- To meet the renewable fuel standard (RFS2) it is critical to understand all potential effects of increasing renewable fuels

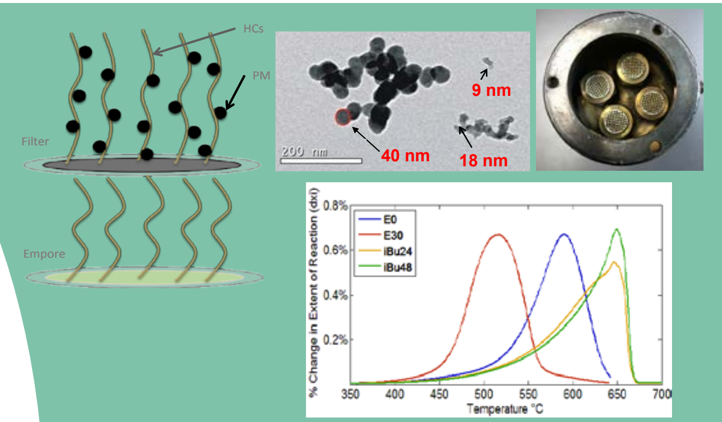
# Approach

**Bring together targeted, engine-based and flow-reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel and lubricant effects and interactions**



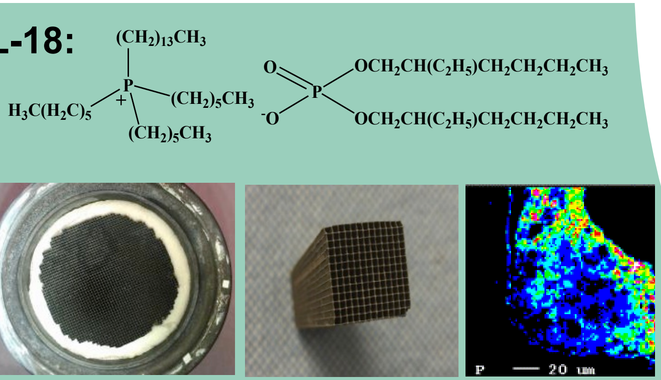

*Emission control opportunities with biofuel blends*



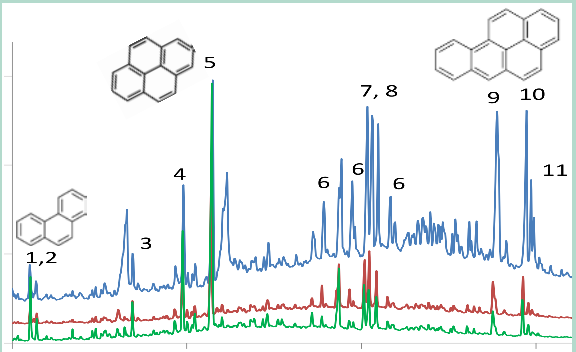




*Fuel and lubricant effects on PM formation in DISI engines*

**IL-18:**




*Compatibility of emerging fuels and lubes with emissions control devices*




*Development of techniques to identify emissions constituents*

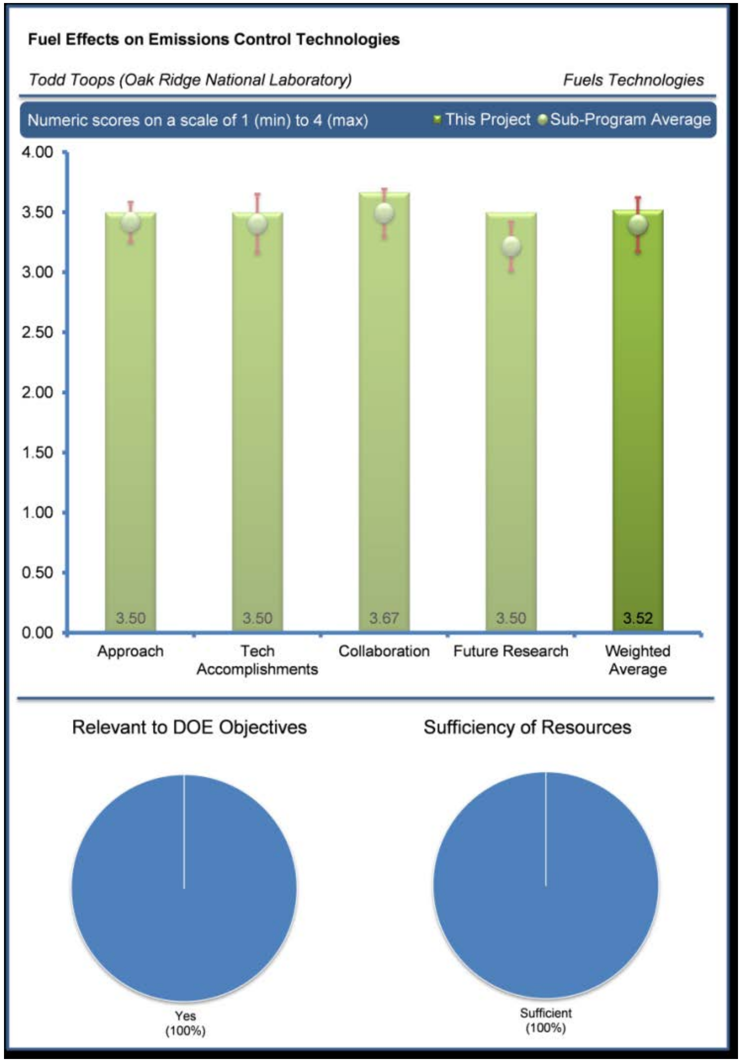
# Collaborators and Partners

- Emissions control opportunities with biofuel blends:
  - Chalmers University, University of Michigan
  - Clean Diesel Technologies, Inc.: catalysts
- Fuel and lubricant formulation impacts on GDI particulate emissions:
  - Umicore: gasoline particulate filter washcoating
  - PNNL: joint collection and characterization campaign
- Compatibility of emerging fuels and lubricants with emissions control devices:
  - NREL, Ford, Cummins, MECA, National Biodiesel Board: Biodiesel-aged collaborative effort
  - GM, Lubrizol, Shell: Ionic liquid development and evaluation

# Milestones

- **Investigation of emissions control opportunities with biofuel blends**
  - ACHIEVED: Present results from engine-based studies of Ag-based catalyst in ethanol SCR approach at CLEERS workshop (6/30/2014)
- **Fuel and lubricant formulation impacts on GDI particulate emissions**
  - ACHIEVED: Describe the influence of biofuel-gasoline blends and lubricant composition on start-stop GDI PM emissions (9/30/2014)
  - ACHIEVED {SMART}: Complete sample collection for particle chemistry and morphology studies from a relevant test platform running at least two different fuels (6/30/2015)
- **Assess Properties, Emissions, and Compatibility of Emerging Fuels and Lubricants**
  - ACHIEVED: Using a suite of novel laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate/orthophosphate interactions with catalytic emissions control (6/30/2014)
- **Compatibility of emerging fuels and lubricants on emissions control devices**
  - ACHIEVED: Through collaboration with NREL, MECA, NBB, and Cummins evaluate impact of long term exposure of biodiesel-based metals in heavy duty configuration. (9/30/2014)
  - ON SCHEDULE {SMART}: Finalize and present conclusive results on the impact of long-term exposure of biodiesel-based metals in heavy duty (6/30/2015)

# 2014 Reviewers (3): Fuel and Lube Emissions Control




***Weighted Average: 3.52***

- **Approach (3.5/4.0)**
  - Comments: in-depth characterization to better understand fuel and lubricant effects has proven to be very successful…developed rapid techniques to move work faster and to lead to more knowledge
- **Technical Accomplishments (3.5/4.0)**
  - Comments: made excellent progress in each of the five research areas on addressing the technical barriers…**significance of the results needs to be pounded home**
  - Response: **this is a focus of technical accomplishments**
- **Collaborations (3.67/4.0)**
  - Comments: very good set of collaborators…provide *excellent* coordination for a successful project
- **Future plans (3.5/4.0)**
  - Comments: continue to address the barriers of inadequate data and predictive tools for fuel effects on emission control systems as well as the long term impact of fuels on EC…**might be better to focus and go deeper with a smaller set of topics**.
  - Response: **discussing fewer topics this year; projects will be streamlined in FY2016 through lab call**
- **Relevance (100%)**
  - Comments: supportive of developing and understanding EC with advanced engines, lubricants, and fuels…**relevant to petroleum displacement**…identifies concerns of changes in fuels and lubricants including renewable fuels



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# Summary of Technical Accomplishments

- **Emissions control opportunities when using biofuels and biofuel/gasoline blends**
  - Lean gasoline engine experiments confirm potential for lean NOx control with ethanol blends
  - Demonstrated Isobutanol (iBu) has similar lean NOx reduction performance to ethanol
- **Fuel and lubricant formulation impacts on GDI particulate emissions**
  - Determined start-stop does not have a major impact on PM formation on E0 or E30; however, when using iBu24, PM increases overall and during start-stop
  - Fuel chemistry shown to have significant effect on PM chemistry; GDI very different than diesel
- **Techniques for identifying lubricant and fuel species in emissions control devices**
  - Used a suite of laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate/orthophosphate interactions with catalysts
- **Compatibility of ionic liquid (IL) lubricant additive with three-way catalysts (TWCs)**
  - Identified P-form on TWC is different when using IL additive compared to ZDDP; aluminum phosphate formation preferred with IL and cerium phosphate with ZDDP
- **Compatibility of biodiesel with diesel emissions control devices**
  - Through collaboration with NREL, Cummins, MECA and NBB completed long-term exposure of heavy-duty emissions control system with full-useful life exposure of Na at ASTM-specified level; full report available shortly*

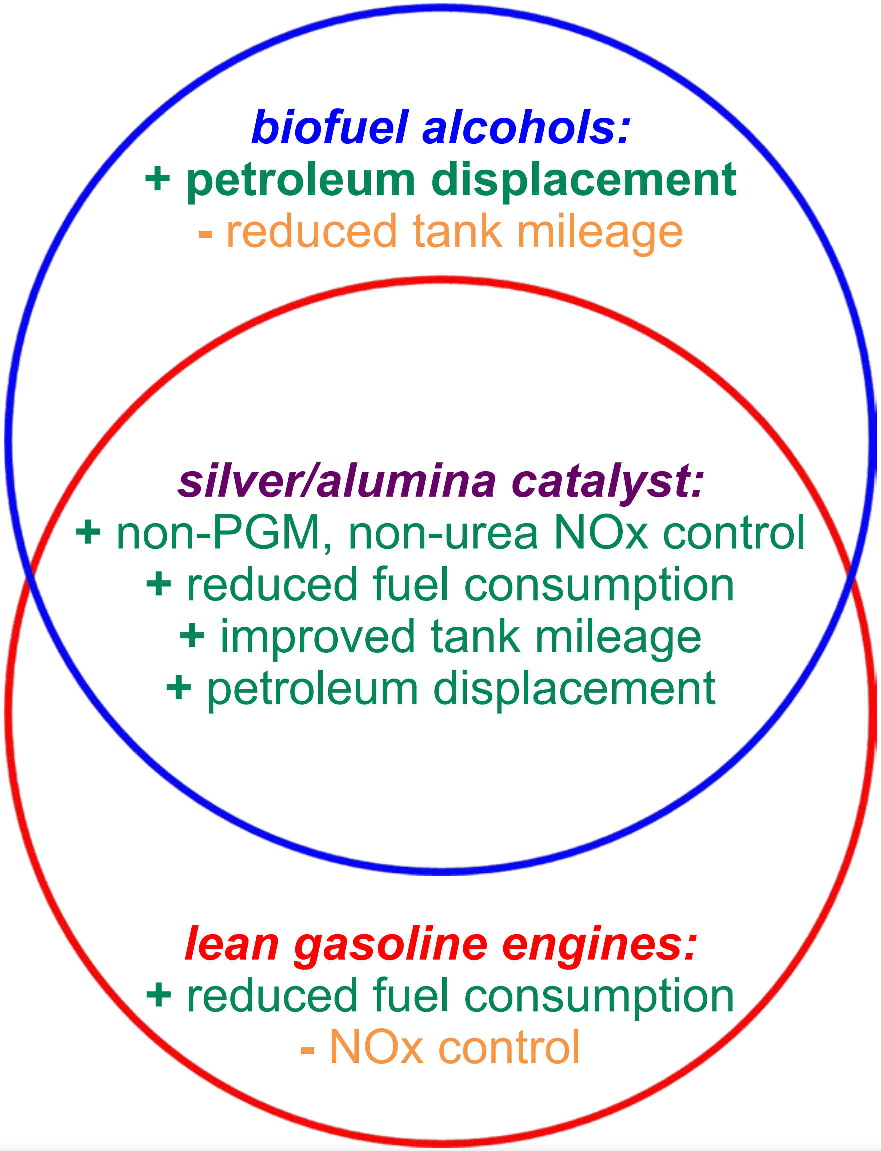
* - details presented by Michael Lance in Advanced Propulsion Materials (PM055)

# Technical Accomplishments

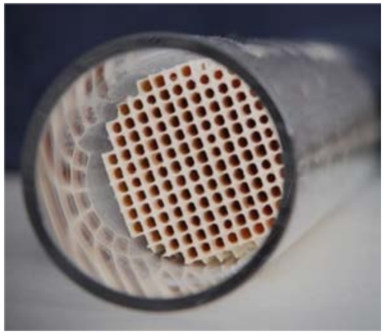
- Emissions control opportunities when using biofuels and biofuel/gasoline blends
- Fuel effects on Gasoline-DI PM
- Compatibility of ionic liquid (IL) lubricant additive with three-way catalysts (TWCs)*
- Techniques for identifying lubricant and fuel species in emissions control devices*
- Compatibility of biodiesel with diesel emissions control devices*

* - briefly discussed in back-up technical slides

# Investigation highlights synergy between biofuels and lean gasoline emissions control

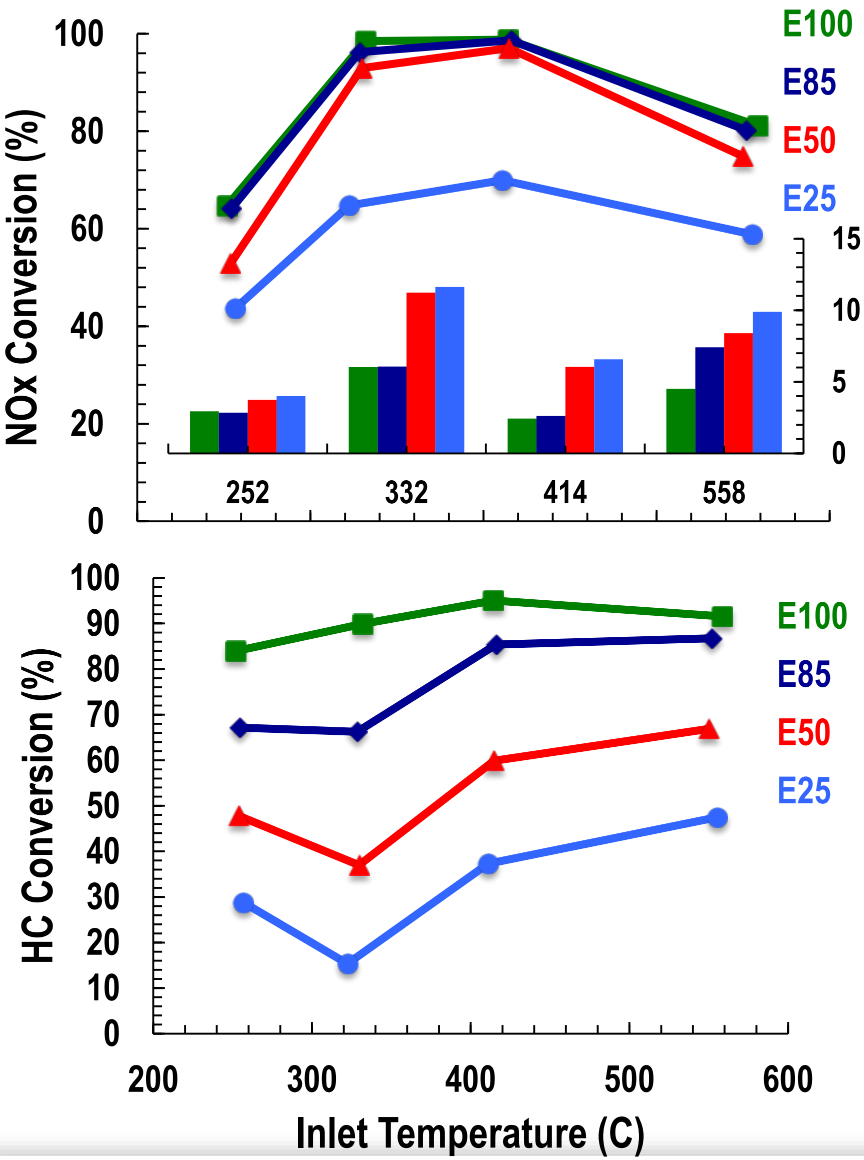



- Conduct preliminary experiments on flow reactor



- Move to lean gasoline engine to evaluate fuel efficiency, NOx conversion in real exhaust

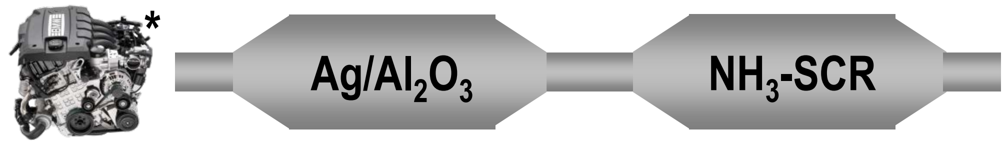

# Lean gasoline engine experiments confirm potential for NOx control with ethanol blends




- Lean gasoline BMW engine experiment
  - steady state operating points selected to achieve range of temperatures, flows

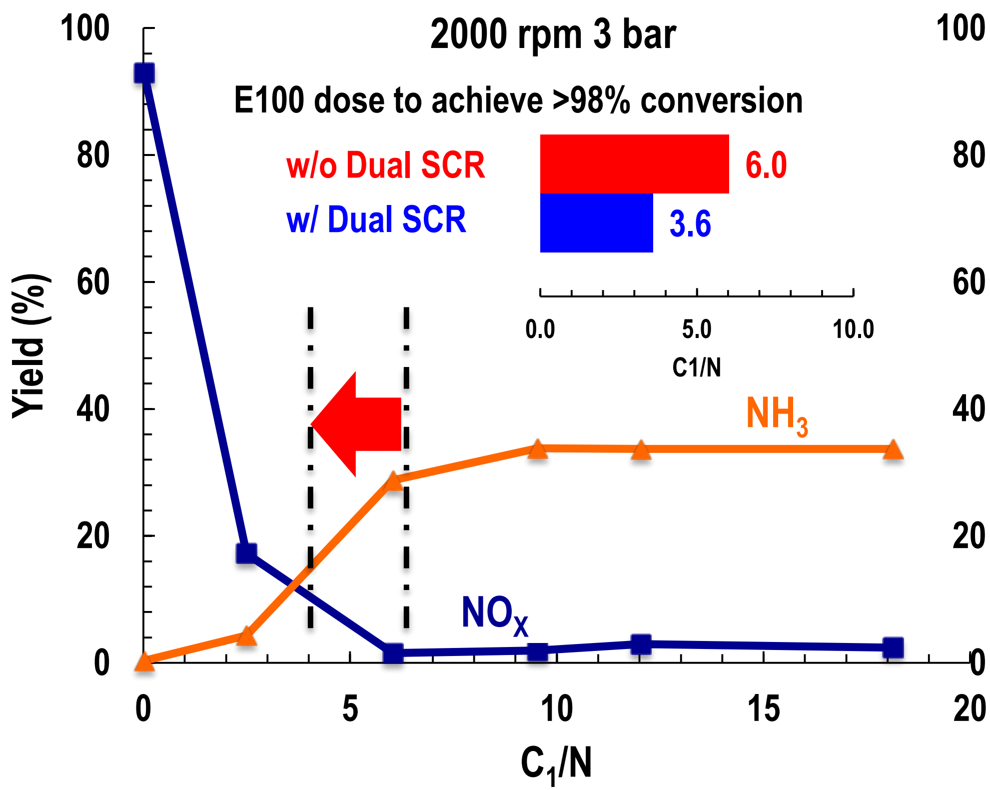
  - in-pipe injection of ethanol/gasoline blends upstream of silver catalyst
- High $NO_X$ conversion achieved with gasoline blends
  - E85 $NO_X$ conversion similar to E100
    - fuel penalties <= 5% for E100, E85
  - E50 still achieves >90% $NO_X$ conversion but at much higher $C_1$/N and fuel penalty
- Higher ethanol content reduces HC slip

# Ethanol + NOx on $Ag/Al_2O_3$ produces $NH_3$ when lean and a Dual SCR† approach can be implemented



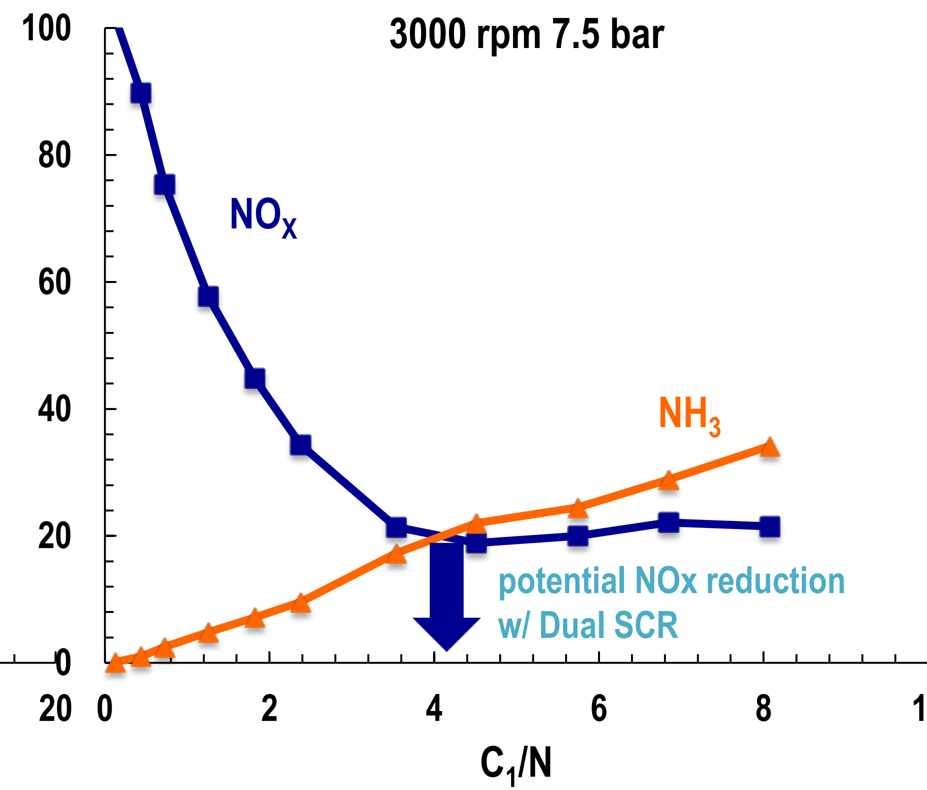

** - engine and catalyst system not to scale*

## Reduced Fuel Penalty




Same $NO_X$ conversion achieved at lower $C_1/N$ by utilizing $NH_3$ with a downstream $NH_3$-SCR

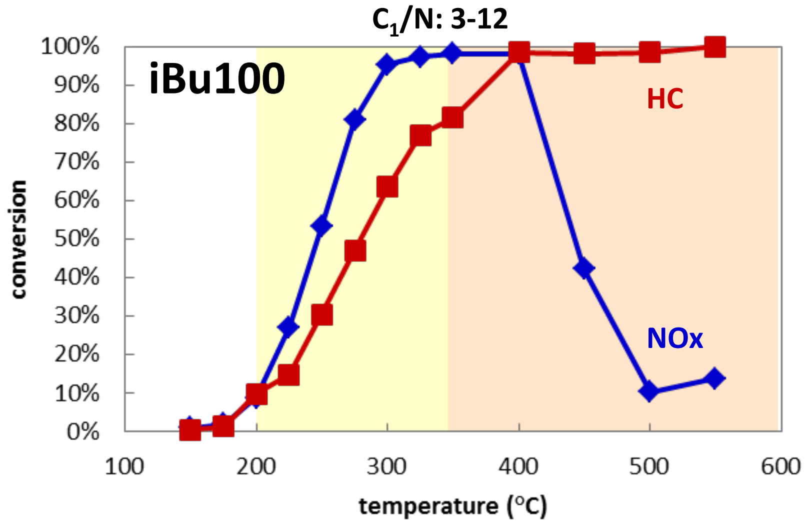
## Increased $NO_X$ Conversion

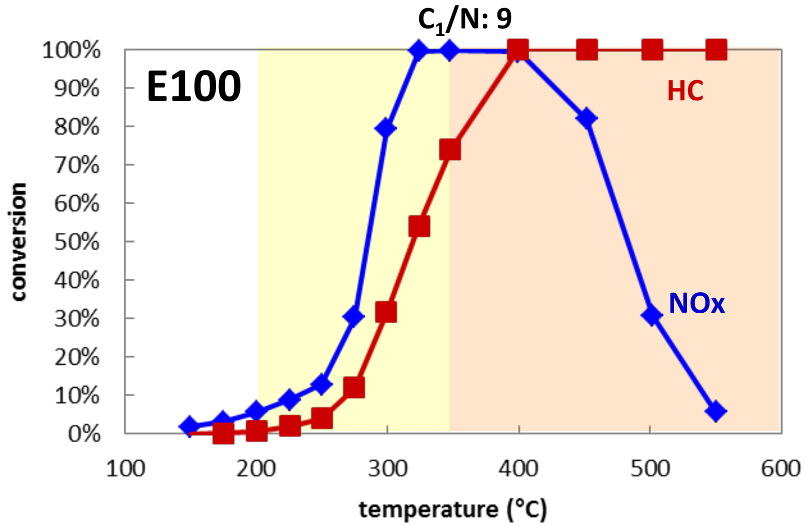



$NO_X$ can further be reduced by $NH_3$-SCR with $NH_3$ generated over $Ag-Al_2O_3$

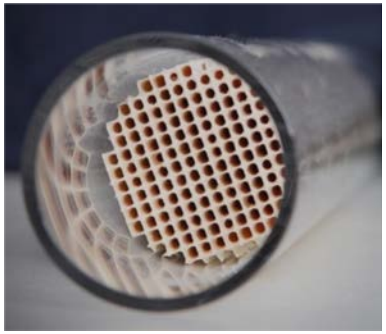
† - *C. DiMaggio et al. SAE 2009-01-0277; G.B. Fisher et al. SAE 2009-01-2818; plus US patent 7,431,905 and 7,399,729 (GE with Tenneco and Umicore).*

# Isobutanol (iBu) shows similar NOx reduction performance to ethanol over silver catalyst




- Flow reactor experiment results
- iBu100 NOx conversion similar to E100 over silver catalyst
  - > 95% conversion over ~100 °C window
  - iBu100 performs slightly better at low temperature
  - similar HC doses required to achieve high NOx conversion



FTP T range: ☐ underfloor ☐ close-coupled

# Significance of findings

- Results continue to indicate potential role of system with ethanol/butanol containing fuels
  - Gasoline blends of both also show relevance
  - gasoline does not negate emissions control chemistry
- Separation membranes for both EtOH and iBuOH could have dual purpose…reductant and high octane in one tank
  - Membranes being investigated to allow a tank with higher octane
  - High octane tank would likely also have higher alcohol content
- Several strategies for improving overall system performance
  - downstream SCR catalyst to take advantage of $NH_3$ production
    - "dual SCR", higher NOx conversion, lower fuel penalty
  - downstream oxidation catalyst for HC cleanup

# Technical Accomplishments

- Emissions control opportunities when using biofuels and biofuel/gasoline blends
- Fuel effects on Gasoline-DI PM
- Compatibility of ionic liquid (IL) lubricant additive with three-way catalysts (TWCs)*
- Techniques for identifying lubricant and fuel species in emissions control devices*
- Compatibility of biodiesel with diesel emissions control devices*

* - briefly discussed in back-up technical slides

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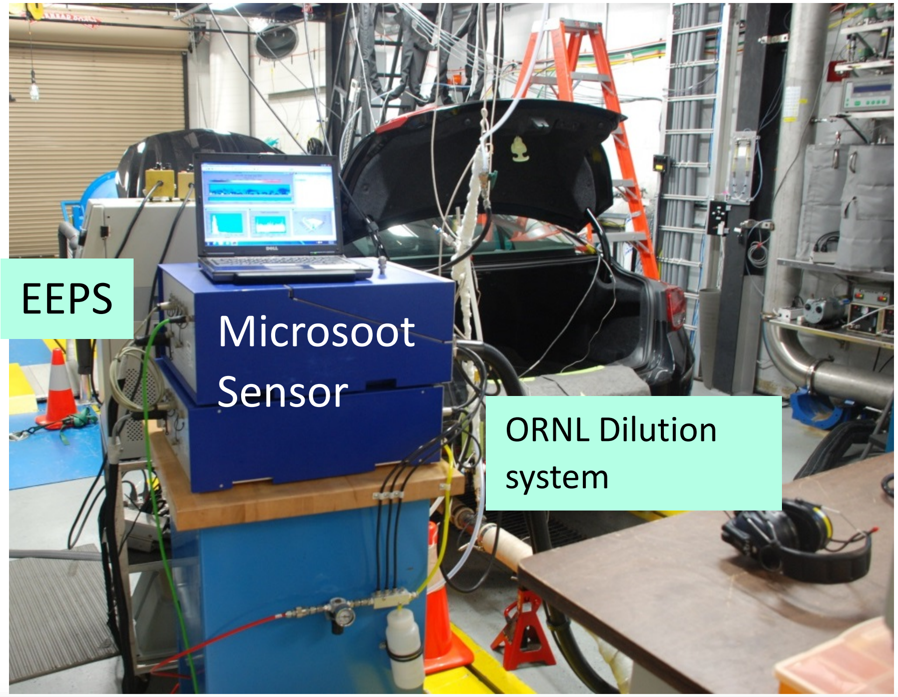
# GDI start-stop emissions measured with bio-fuel blends

***Will fuel saving technology of start-stop impact GDI PM emissions?***

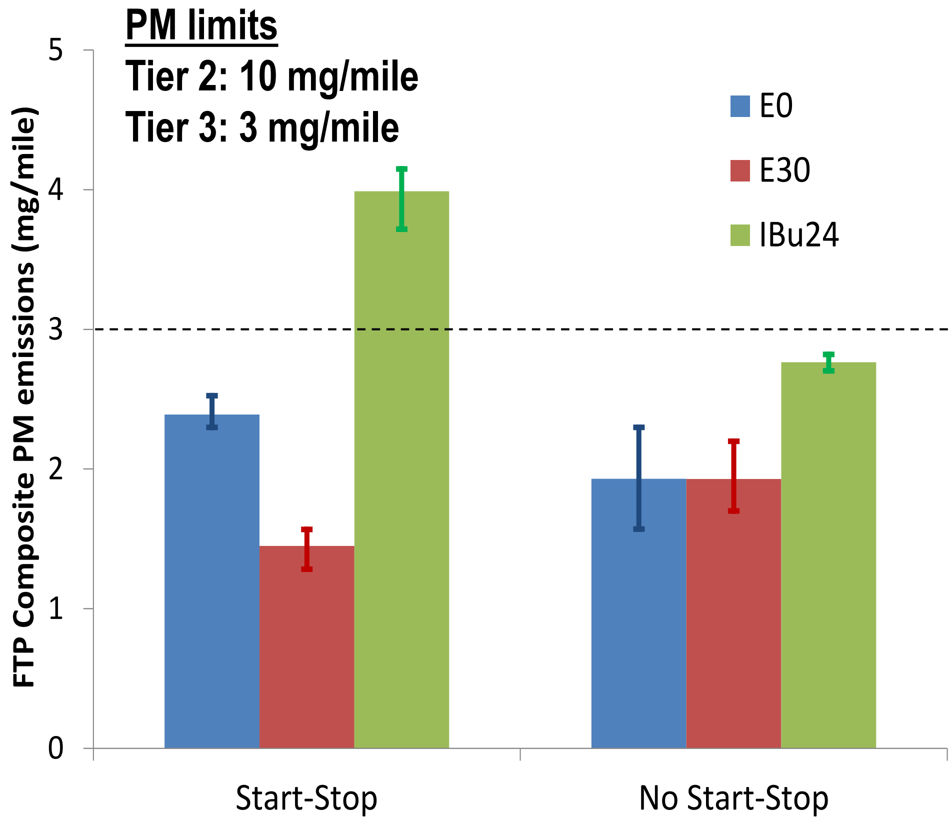
- Previously observed highest PM during cold start of FTP
  - Enrichment for ease of starting and cold surfaces likely causes
- Obtained and evaluated Malibu e-Assist vehicle
- Complements ongoing work because any gasoline particulate filter will capture the most PM during startup
- Focus on fuel oxygen effect on PM mass and size
  - E0, E30, iBu24



# E30 fuel has lowest measured PM and PAH; unaffected by Start-Stop

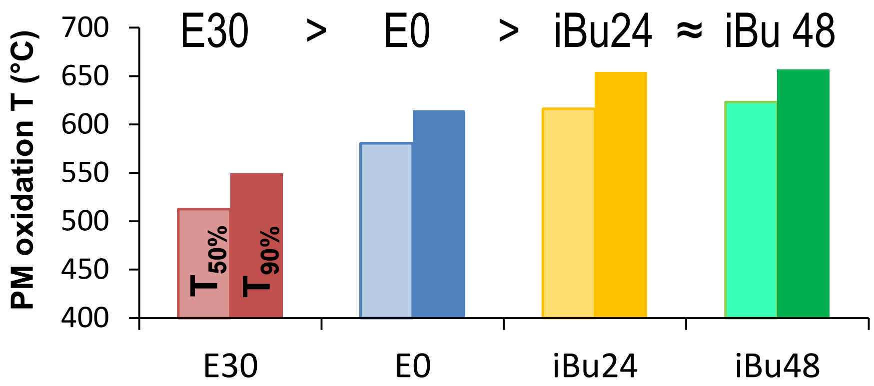
***Does Start-Stop increase PM Emissions?***

- Start-Stop vs. no Start-Stop:
  - Start-Stop FTP mass results show significant increase only for iBu24
  - Start-Stop soot emissions decrease with successive hot starts
- Gasoline vs. alcohol fuels:
  - Real-time soot shows "spikes" are higher, mass is higher with iBu24

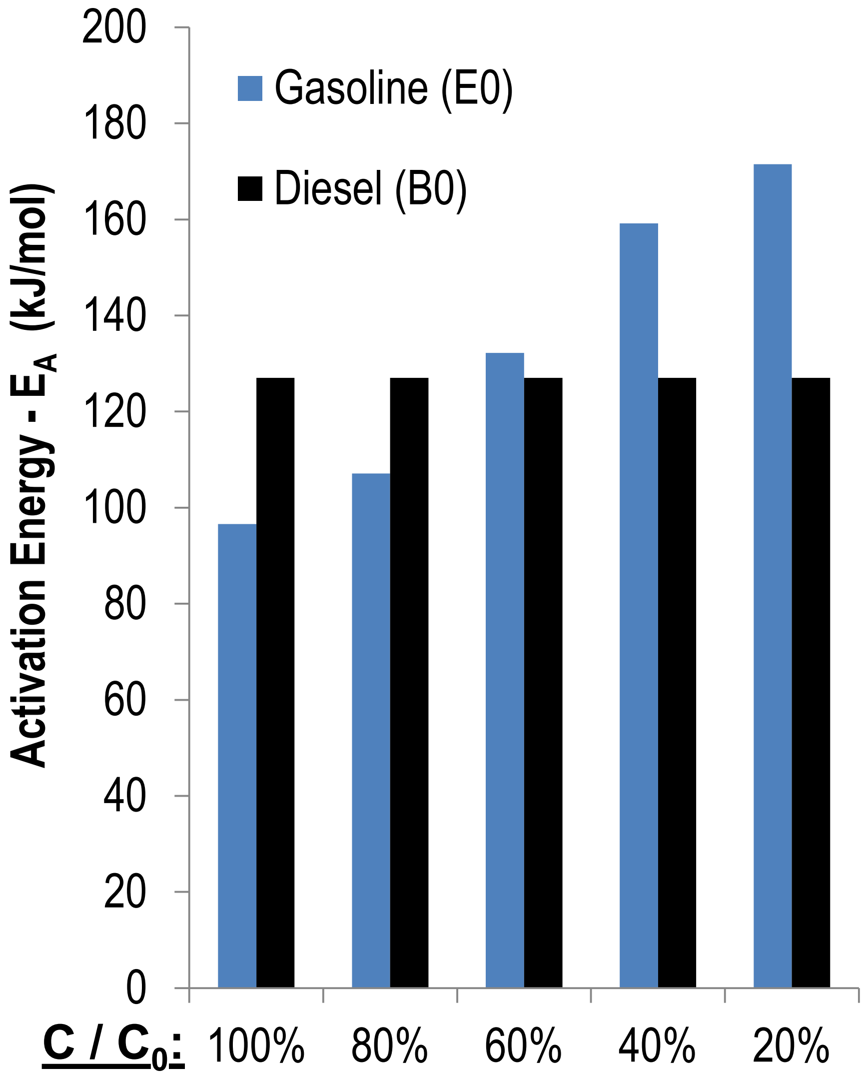


# PM chemistry significantly affected by fuel-blend; GDI soot oxidizes differently than diesel soot

- **Impact of Fuel Blend on PM Reactivity**



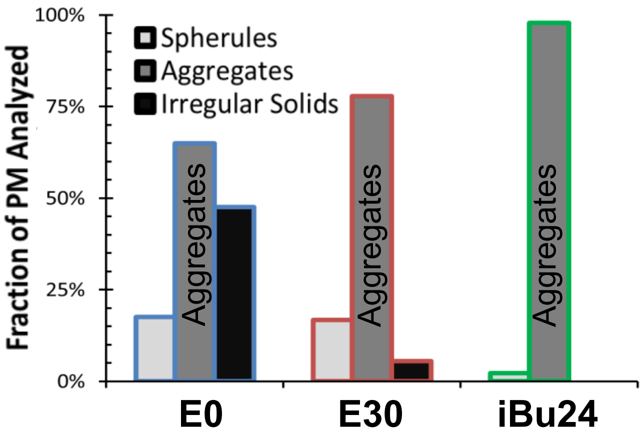

- **Soot kinetics studies in progress**
  - Pulsed oxidation allows control of soot consumption…and access to kinetics
    - Activation energy (Ea) throughout oxidation
  - GDI-based soot reacts differently than diesel
    - GDI (E0): Ea ***increases*** (97 to 170 kJ/mol)
    - Diesel: same Ea throughout (127 kJ/mol) *
  - *Implication*: GDI soot is progressively more difficult to oxidize; higher temperatures or longer regeneration times needed…more fuel



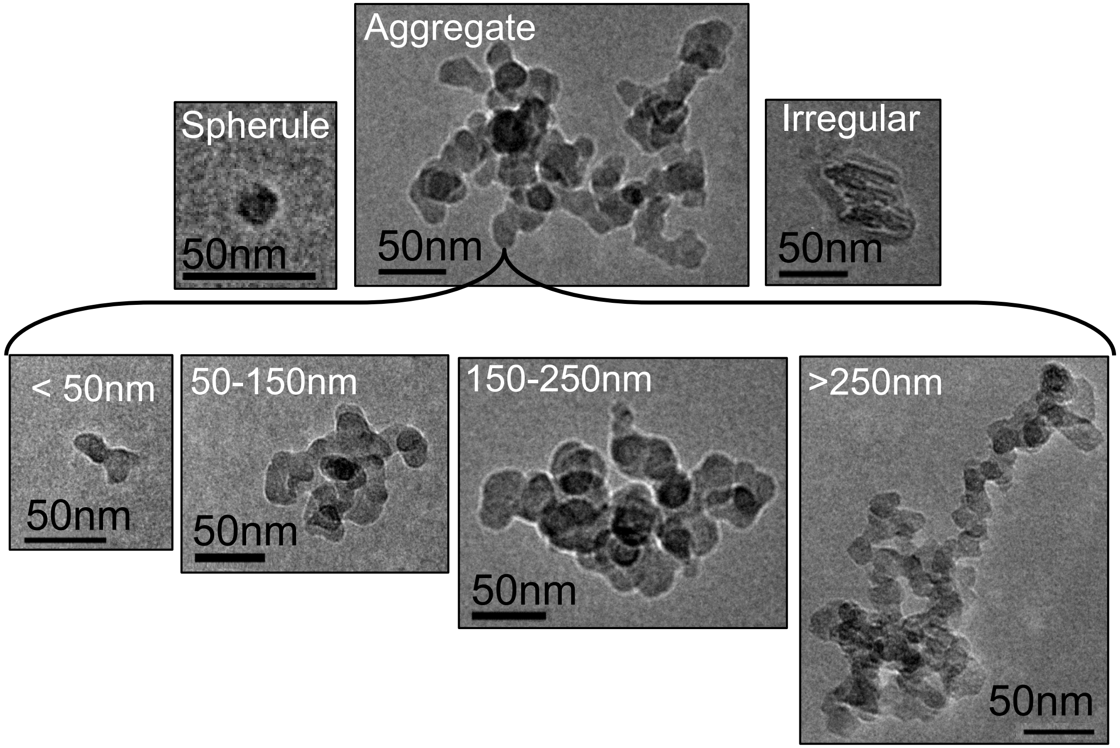

* - Pihl. J.A.; Lewis, J.A.; Toops, T.J.; Adelman, B.J.; Derybowski, E.M. (2013) Top. Catal. 56:499-503.

# Fuel-blend also impacts PM morphology and size

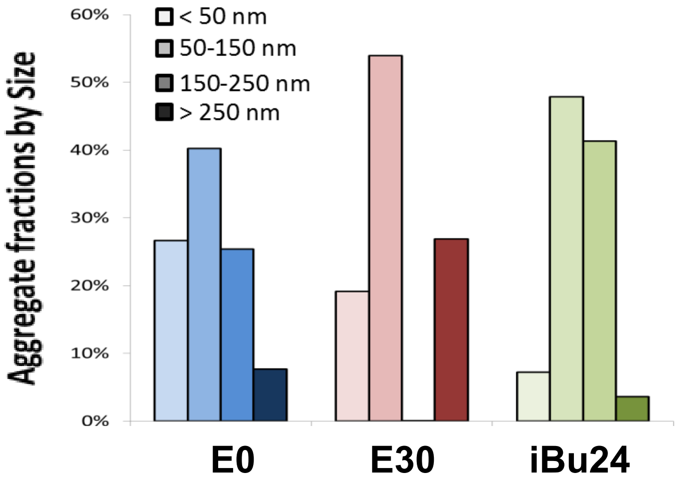
## PM Morphology




- Fuel-blending impacts variability of GDI PM morphology
  - E0 has highest variability in PM morphology
  - E30 & IBu24 primarily form aggregates




## Aggregate-PM Size Distribution




- E0 aggregate size distribution has smaller overall, but more evenly distributed than E30 and iBu24
- Oxygenated fuel blends (E30 & iBu24) have PM sizes that favor larger aggregates

# Significance of findings

## *Does Start-Stop increase PM Emissions?*

- Minimal impact observed from start-stop for E0 and E30

## *Is there a fuel effect in Start-Stop PM?*

- Only iBu24 demonstrated effect from start-stop operation
- Overall effect on PM emissions: iBu24 > E0 > E30

## *Does fuel chemistry affect PM oxidation?*

- PM reactivity…yes: E30 > E0 > iBu24 ≈ iBu48
  - E0 and E30 PM likely to oxidize through standard operation
  - …not necessarily true for iBu24 and iBu48
- GDI-based soot is very different than diesel
  - Full regeneration may be difficult or require more energy

## Remaining Challenges | Future Directions

- **Emissions control opportunities when using biofuels and biofuel/gasoline blends**

| Remaining Challenges | Future Directions |
| --- | --- |
| *Unknown durability effects; can membrane be employed to provide a ethanol/biofuel source?* | Sulfur and thermal exposure; identify membranes of interest and evaluate separation potential with biofuel blends |

- **Fuel and lubricant formulation impacts on GDI particulate emissions**

| Remaining Challenges | Future Directions |
| --- | --- |
| *Will the fuel-derived differences in soot chemistry affect GPF control strategies?* | Complete PM kinetic study w/ E30 & iBu24; translate findings to reaction parameters |

- **Techniques for identifying lubricant and fuel species in emissions control devices**

| Remaining Challenges | Future Directions |
| --- | --- |
| *Are species found in accelerated phosphorous addition relevant to lubricant phosphorous?* | Complete extraction analysis on the components; compare to engine samples |

- **Compatibility of ionic liquid (IL) lubricant additive with three-way catalysts (TWCs)**

| Remaining Challenges | Future Directions |
| --- | --- |
| *Is 2nd generation IL also compatible with TWCs? Are diesel EC components affected?* | Gasoline and diesel durability studies with new ILs and stable engine platforms |

- **Compatibility of biodiesel with diesel emissions control devices**

| Remaining Challenges | Future Directions |
| --- | --- |
| *If heavy duty evaluation suggests that Na levels are too high, can standards be lowered?* | Confirm findings on emissions and EC devices and report to stakeholders |

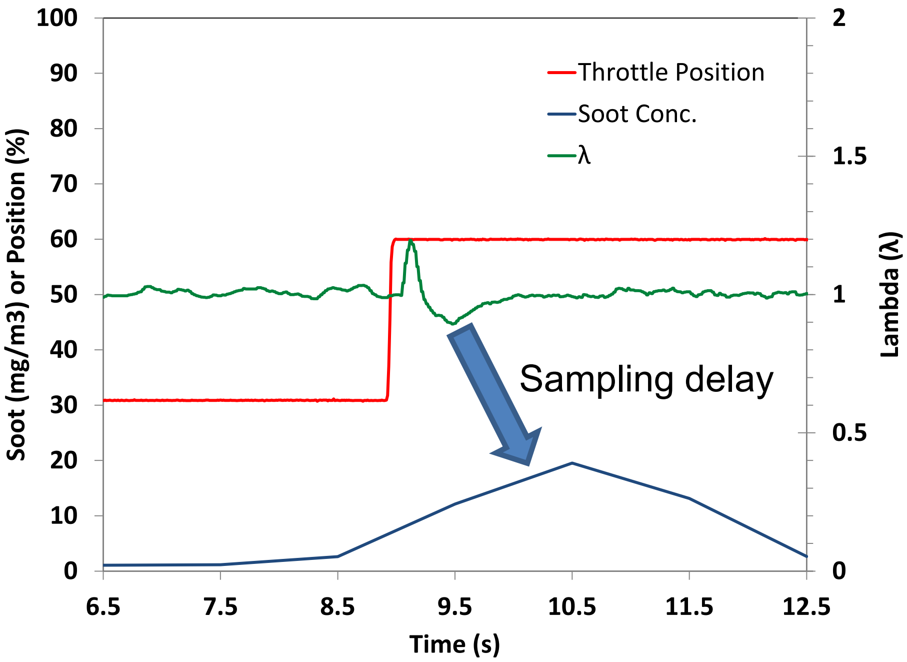
# Summary

- Relevance: These studies are targeted towards providing data and predictive tools to address gaps in information needed to enable increased use of biofuels
- Approach: Targeted, engine-based and flow-reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel and lubricant effects
- Collaborations: Wide-ranging collaboration with industry, academia, and other national labs designed to maximize impact and lead to marketable solutions
- Technical Accomplishments:
  - Lean gasoline engine experiments confirm potential for lean NOx control with ethanol blends
  - Demonstrated Isobutanol (iBu) has similar NOx reduction performance to ethanol
  - Determined start-stop does not have a major impact on PM formation on E0 or E30
  - Fuel chemistry shown to have significant effect on PM chemistry; GDI very different than diesel
  - Used a suite of laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate/orthophosphate interactions with catalysts
  - Established durable engine platform for well-controlled and repeatable TWC exposure to fuels and lubricant additives; being employed with second generation IL-additive
- Future Work: well-designed plans in place to address remaining barriers; guidance from industry incorporated into future directions

# TECHNICAL BACKUP SLIDES

# GDI soot from "acceleration" point not steady-state operation; primary source of real PM generation

- GDI stoichiometric engine operated to mimic "tip-in" point of acceleration
  - novel approach designed to capture mode of maximum PM generation*
  - Brief period of rich operation (λ = 0.91) , medium-high load
- Specific focus on fuel oxygen effect on PM characteristics
  - E30, IB48; equivalent fuel oxygen content
  - Collect small particulate filter (GPF) cores
    - Soot oxidation kinetics/behavior critical for GPF design/performance
    - Fuel oxygen important for diesel soot oxidation
    - Sample holder with four 1" GPFs
      - allows repeated measurements
  - Oxidize in flow reactor



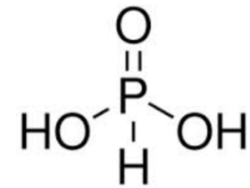

* - measured PM with PNNL collaboration: ACE023

# Method developed to introduce different forms of phosphorous onto catalysts to examine effects

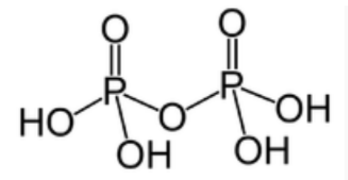
- Developed lab-based approach to introduce phosphorous compounds
  - Initial form may vary with lube
- Furnace based technique with nebulizer-based introduction (mist)
  - syringe pump w/ coaxial capillary/SS-sheath at cat-inlet
- Full DOC exposed but only front section evaluated for effects (red)
- Does initial phosphate species effect the extent of DOC deactivation? Is technique useful?

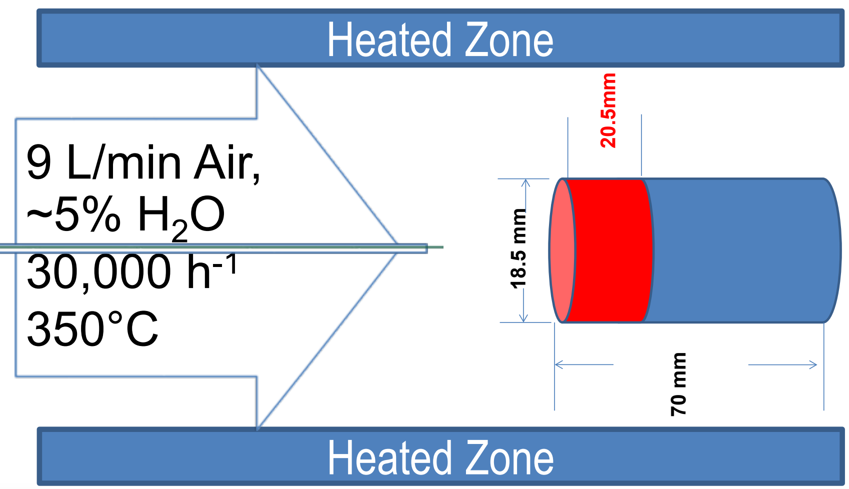
**Two phosphorous compounds used:**

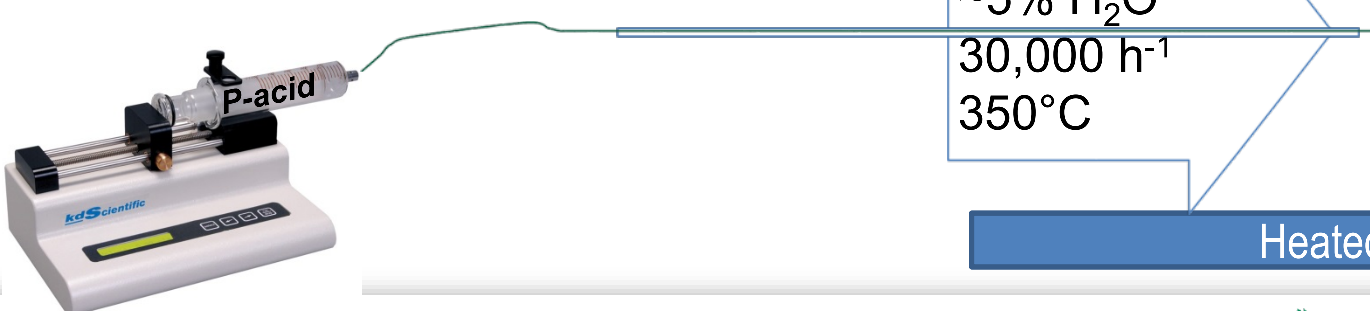
1. Mono-phosphoric acid ($H_3PO_3$)




2. Di-phosphoric acid ($H_4P_2O_7$)



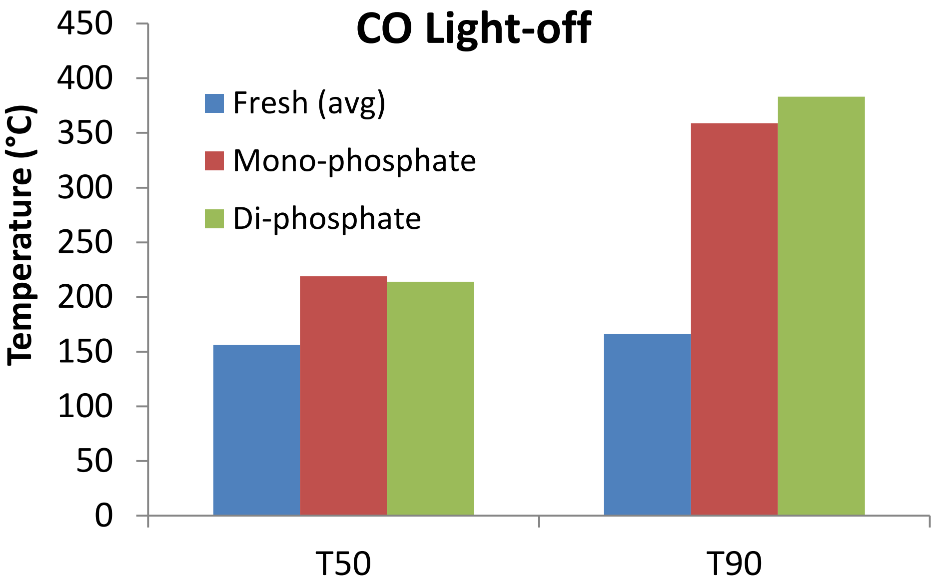



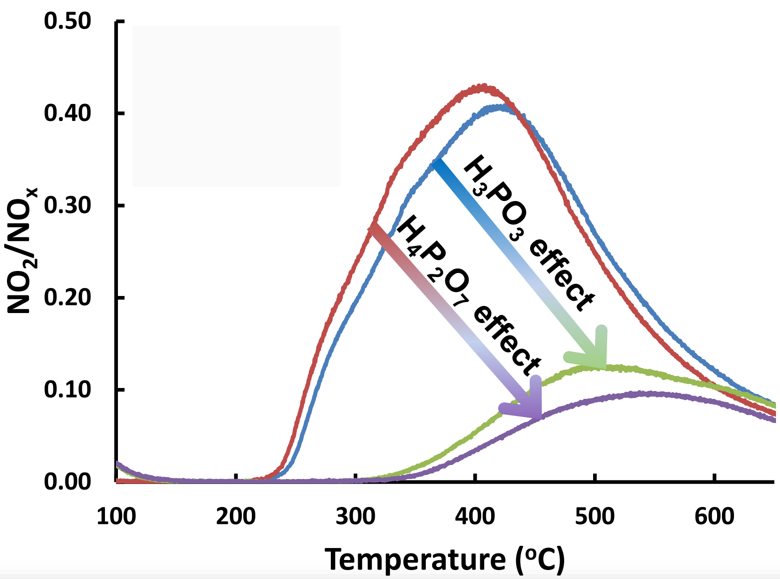



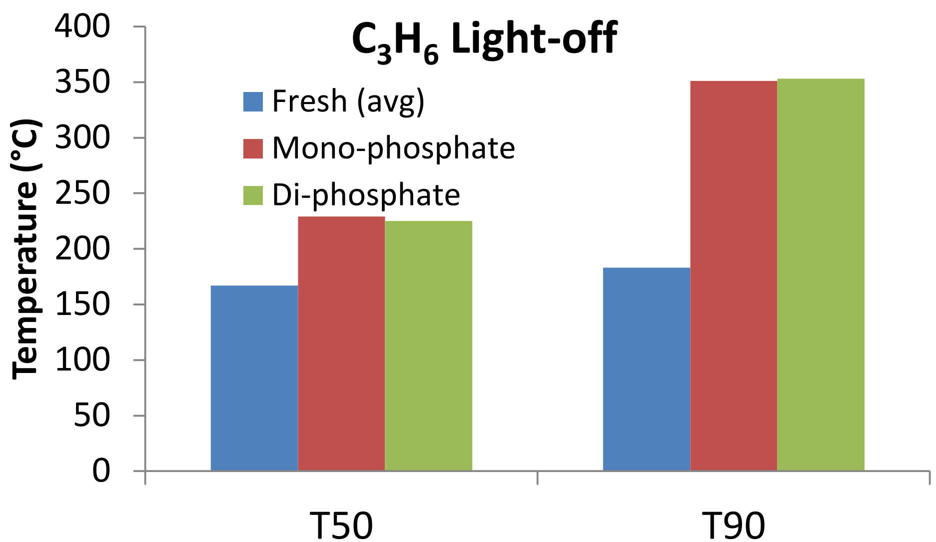

*Syringe pump image from* ***©2015 Stoelting Co.*** *(http://www.stoeltingco.com/)*

# TWC affected by P-exposure, but not initial P-species

- Deactivation is clearly observed
  - P exposure delayed CO and $C_3H_6$ conversion
  - Less NO converted for P exposed catalyst
- Minimal differences between the mono- and di-phosphate
  - Di-phosphate may have a marginal greater impact

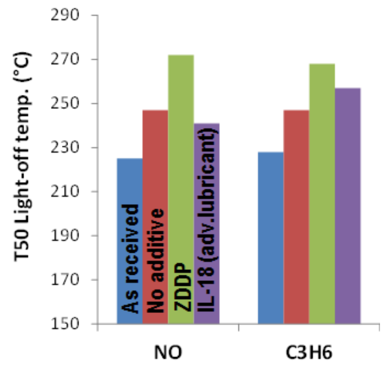


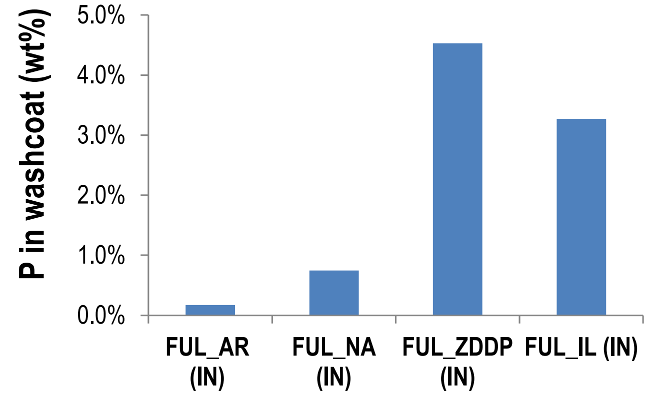



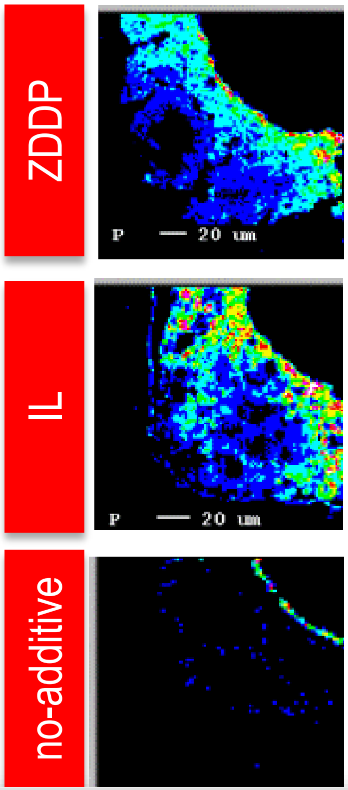



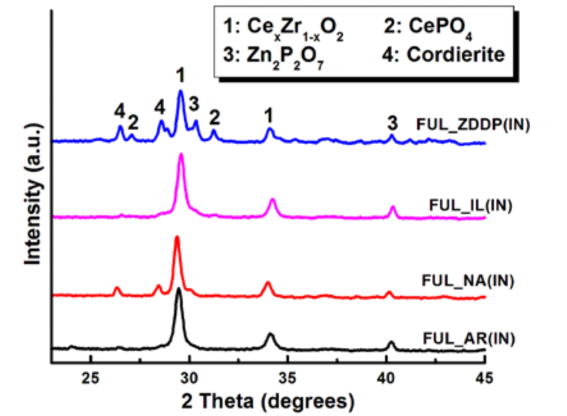
# IL-based P interacts with TWC differently than ZDDP-based P

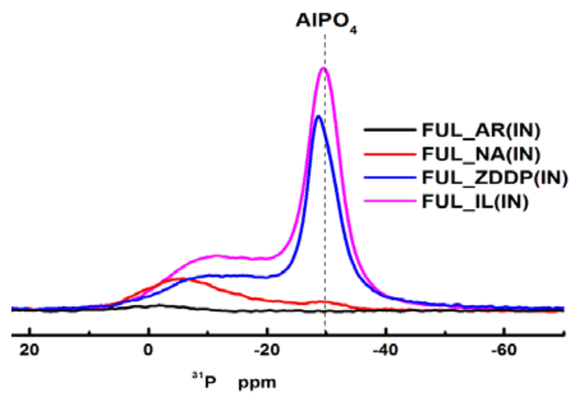
- IL-aged TWCs consistently less-impacted than the TWCs aged with ZDDP
  - Light-off temperature, water-gas-shift reactivity and oxygen storage measured
- The IL-aged TWCs had significant P, but the interactions with the TWC components were less severe
  - P more water soluble on the IL-aged TWC
  - No formation of cerium phosphate
  - No observation of an overlayer with IL-aged samples
  - With IL, formation of aluminum phosphate ($AlPO_4$), rather than ceria phosphate ($CePO_4$), appears to be the preferred form of P in TWC
    - minimizes impact



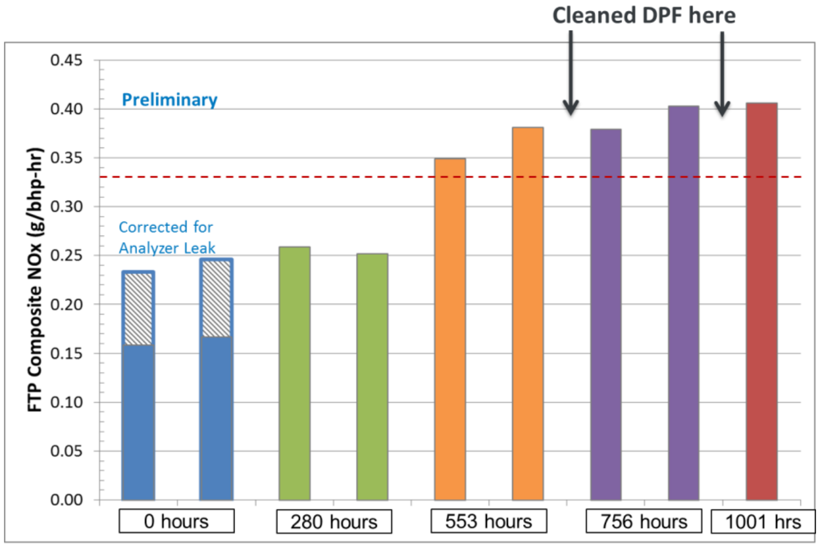



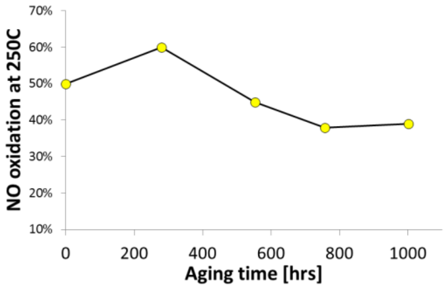



# Biodiesel compatibility with modern emissions control devices; impact of fuel-borne metals

- Study aimed at evaluating the impact of fuel-borne Na on emissions control systems
- Current focus is on Heavy Duty system
  - Cummins ISL: DOC→DPF→SCR
  - 435,000 mile equivalent thermal/Na exposure
    - Completed in 1000h vs. 22,000h; Na content: 14x Na
  - NREL, Cummins and ORNL collaboration
  - MECA, EMA and NBB heavily involved
  - After 500 hours, NOx emissions are over limit
  - Replacing aged components with degreened ones suggest NOx failure is compound problem:
    - 65% of losses due to DOC+DPF feed gas effect
      - NO to $NO_2$ deactivation
    - 35% due to degraded SCR; likely thermal aging
- Parts are currently at Cummins and ORNL for post –mortem analysis to differentiate effects of P (lubricant) and Na
  - Initial results: Na primarily in the DOC and DPF; not SCR
  - P may be primary deactivation on DOC
  - Ash build-up in DPF being investigated as well




- *DOC NO to $NO_2$ oxidation decreases after 500h (50% FUL)*
- *EPMA data shows Na saturates DOC at 500h*
- *Minimal Na in SCR*