Fuel and Lubricant Effects on Emissions Control Technologies

Todd J. Toops

John Storey, Mary Eibl, Sam Lewis, Josh Pihl, Chao Xie, Melanie DeBusk, Vitaly Prikhodko, James E. Parks II, Michael Lance

Oak Ridge National Laboratory

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DOE Management Team:
Steve Goguen, Kevin Stork and Steve Przesmitzki
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
  - GM, Ford, Cummins, MECA, CDTi, NBB, Umicore, Biodiesel Steering Committee
- National Laboratories
  - NREL, PNNL
- Academic
  - University of Michigan, Chalmers University

Budget

- Funding received in
  - FY13: $700K
  - FY14: $825K
- 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

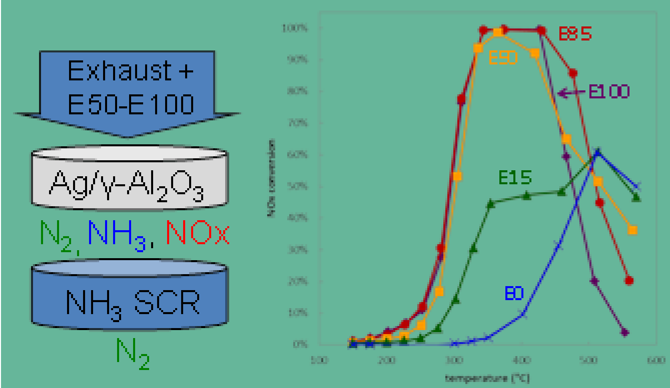
- Provide data to elucidate fuel-property impacts on emissions and emissions control systems
- Identify or alleviate concerns associated with changes in fuels and new lubricants
  - including renewable fuels (alcohols and FAME are current primary focus)
- Investigate unique characteristics of fuels that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

Relevance:

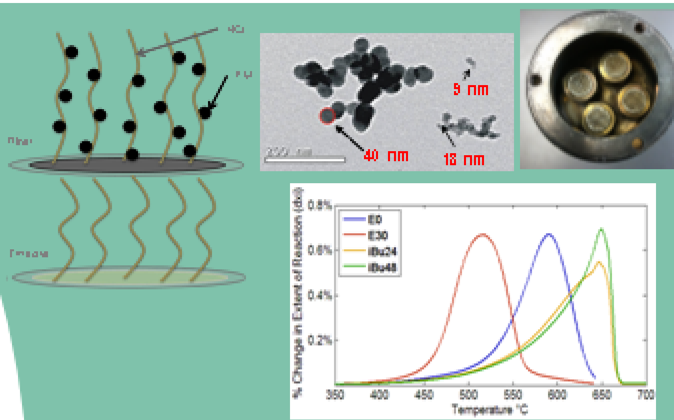
- Addresses Fuels Technology barriers D and E:
  - Inadequate data for fuel effects on emissions and emission control system
  - Inadequate data on long-term impacts of fuel and lubricants on emission control systems.
- To meet the renewable fuel standard (RFS2) it is critical to understand all potential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

Approach

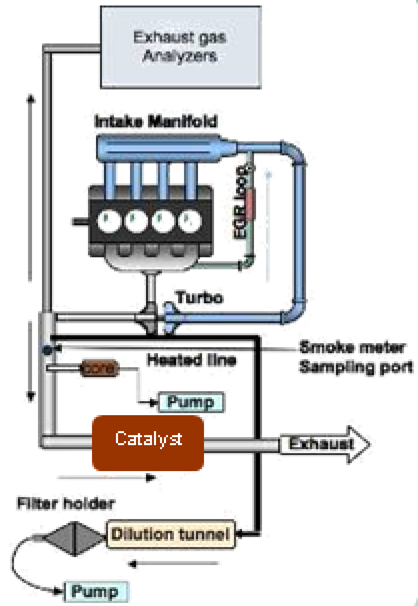
Bring together targeted, engine-based and flow-reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel and lubricant effects and interactions



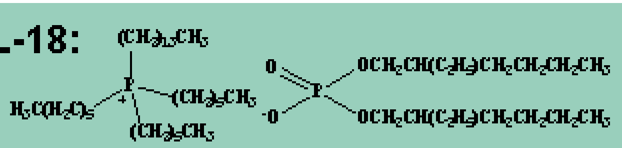
Emissions control opportunities with biofuel blends

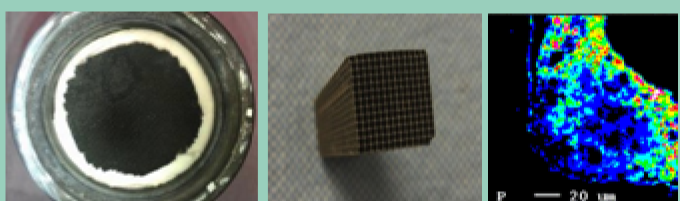


Fuel and lubricant effects on PM formation in DISI engines

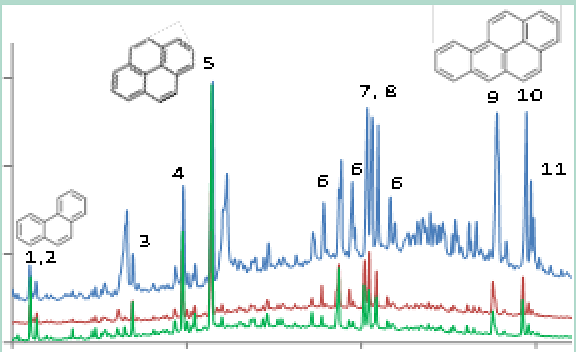


IL-18:





Compatibility of emerging fuels and lubes with emissions control devices



Development of techniques to identify emissions constituents

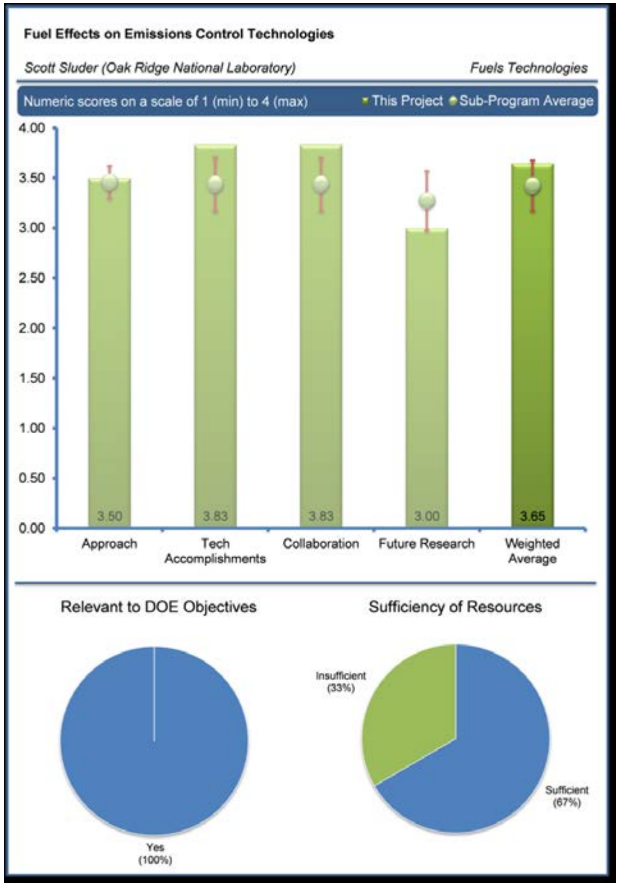
Collaborators and Partners

- Emissions control opportunities with biofuel blends:
  - Chalmers University, University of Michigan
  - Clean Diesel Technologies, Inc.: catalysts
    - Formerly Catalytic Solutions, Inc.
- 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: Ionic liquid development and evaluation

Milestones

- **Investigation of emissions control opportunities with biofuel blends**
  - ACHIEVED: Demonstrate capability of reductant supply for catalysts on lean gasoline engine research platform (12/31/2013)
  - ON SCHEDULE: 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**
  - ON SCHEDULE: Describe the influence of biofuel-gasoline blends on start-stop GDI PM emissions (9/30/2014)
  - ON SCHEDULE: Describe the influence of lubricant composition on start-stop GDI PM emissions (9/30/2014)
- **Assess Properties, Emissions, and Compatibility of Emerging Fuels and Lubricants**
  - ON SCHEDULE: 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**
  - ON SCHEDULE: 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)

Responses to 2013 Reviewers' (5) Comments



Many comments on EGR cooler project that ended last year and thus not addressed here

- **Approach (3.5/4.0)**
  - Comments: permits significant new knowledge generation…unclear how results address the barrier of inadequate predictive tools
  - Response: modeling and predictive tools are not key focus here; however, modelers utilize our results in their predictive tools*
- **Technical Accomplishments (3.8/4.0)**
  - Comments: accomplishments have been made in several areas …definitely a benefit to OEMs, as well as their customers
- **Collaborations (3.8/4.0)**
  - Comments: wide-ranging collaboration with industry, academia, and other labs…should lead to marketable solutions
- **Future plans (3.0/4.0)**
  - Comments: future research appropriate and builds on past work…hope proposed P research takes into account earlier studies…consider the peculiar FAME profile of algal biofuel
  - Response: P-based studies will build on past studies and use as a comparison point…excellent suggestion on algal fuels; will investigate to determine if a study is warranted
- **Relevance (100%)**
  - Comments: resolution of issues with biofuels decreases dependence on petroleum…project addresses fuel technology barriers

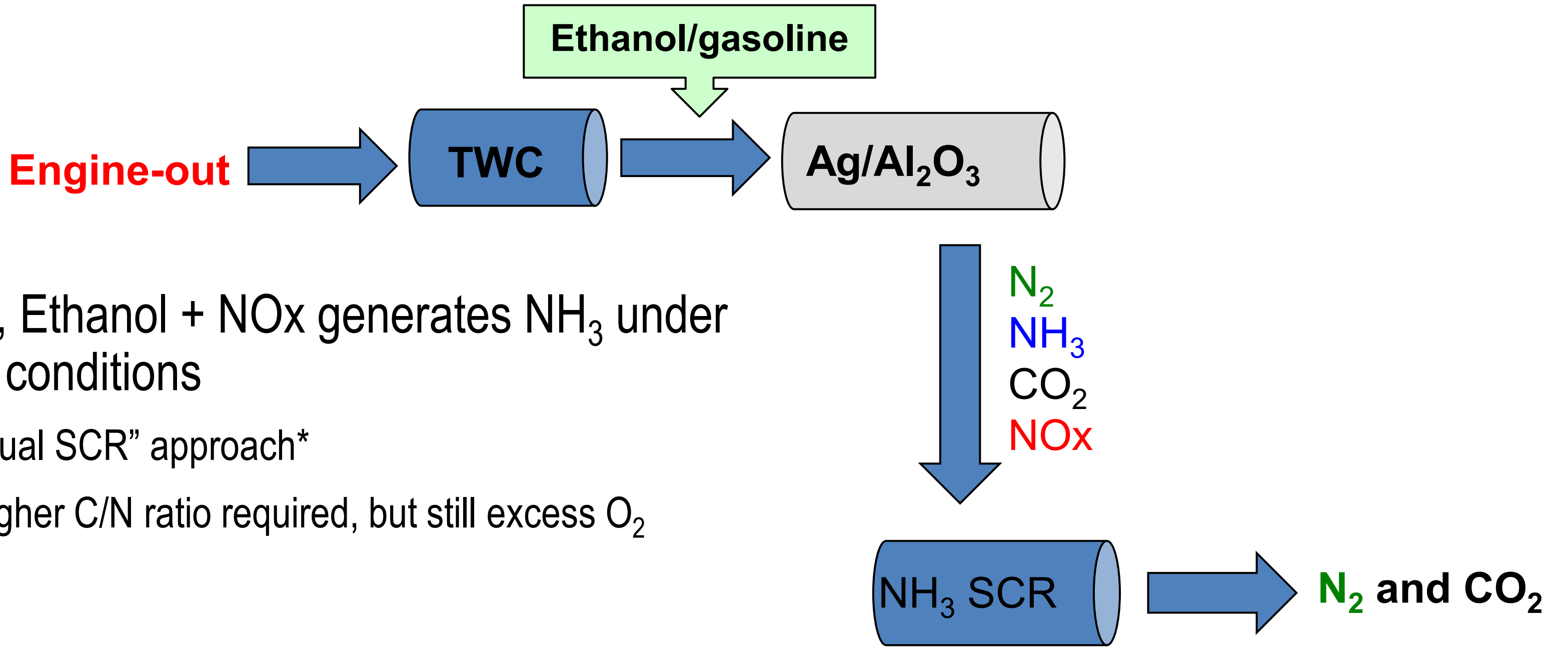
* - M. Abarham et al., Int. J. Heat Mass Trans. 61 (2013) 94-105.

Summary of Technical Accomplishments

- **Investigation of emissions control opportunities with biofuel blends**
  - Showed 95-100% NOx conversion with E50 and E85 in flow reactor; E85 better than E100
  - Established evaluation capability on lean gasoline engine platform
- **Fuel and lubricant formulation impacts on GDI particulate emissions**
  - Designed novel approach to realistically capture mode of maximum PM generation
  - Determined PM chemistry significantly affected by fuel-blend
- **Assess Properties, Emissions, and Compatibility of Emerging Fuels and Lubricants**
  - Developed size-resolved PM sampling method and direct thermal analysis method that avoids problems with solvent extraction and has much higher sensitivity
  - Developed sampling and extraction method for identifying nitro-organics formed in novel combustion regimes with biofuels
- **Compatibility of ionic liquid (IL) lubricant additive with three-way catalysts (TWCs)**
  - Demonstrated IL-based lubricant has moderately less impact on TWC reactivity than ZDDP
- **Compatibility of biodiesel with diesel emissions control devices**
  - Determined acceleration factor of 14 x was justifiable for long term evaluation and that 28x falsely accelerates aging; 1000h heavy-duty durability exposure commenced

Ethanol and Ag/Al_2O_3 offer opportunity for low-cost lean emissions control of NOx

- Silver on alumina (Ag/Al_2O_3) catalysts for NOx control
  - Alcohols, especially ethanol, effective biofuel reductants for HC-SCR of NOx
  - Potential for lean gasoline applications
- Ethanol present in gasoline and "E85" available at many stations
- LOW COST: Silver is ~1/70th the cost of platinum

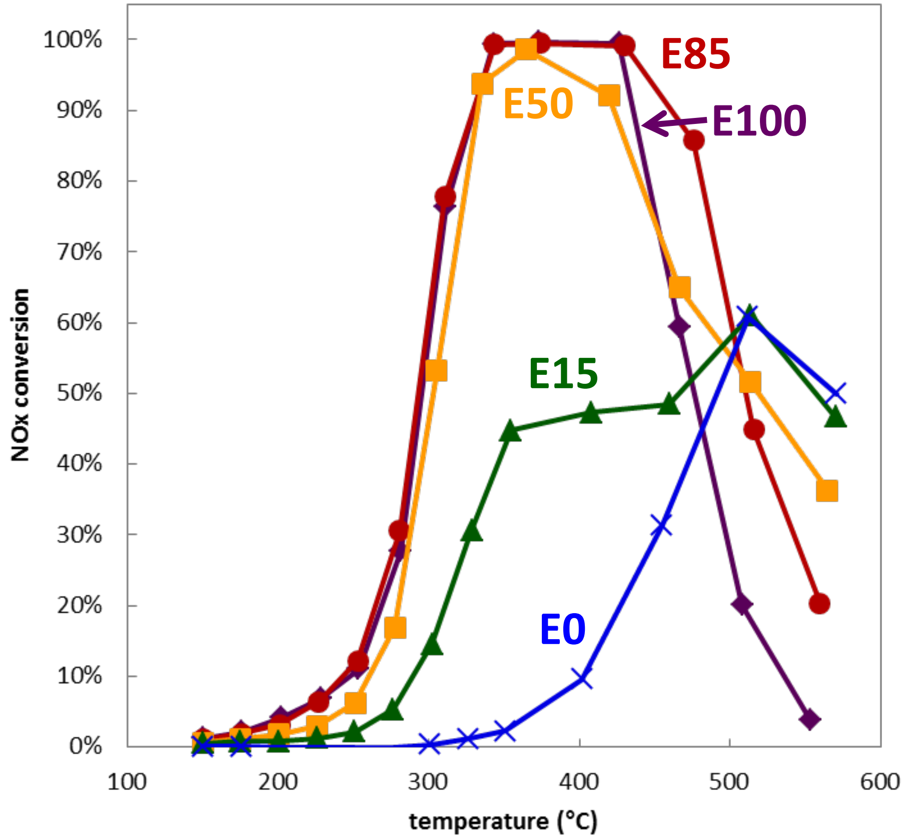


- ALSO, Ethanol + NOx generates NH_3 under LEAN conditions
  - "Dual SCR" approach*
  - Higher C/N ratio required, but still excess O_2

* - 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)

Ethanol/gasoline blends show good activity for SCR of NO over a silver/alumina catalyst

- Experiments conducted on a flow reactor
  - 2 wt% Ag/Al_2O_3 (CDTi)
  - fuel blends mixed from 200 proof ethanol and EEE-Lube Cert Gasoline
- Ethanol active for NOx reduction even when mixed with gasoline
  - E85 better than E100
  - E50 still achieves >90% conversion
  - lower blends: separation membrane?
- Future work:
  - evaluate with isobutanol and E30
    - Renewable super premium
  - move to engine evaluation (started)
    - Using lean-gasoline engine platform
  - evaluate durability; sulfur and thermal



In back-up technical slides:

- NH_3 generation highest with E85 and E100
- Low N_2O formation; decreases with EtOH

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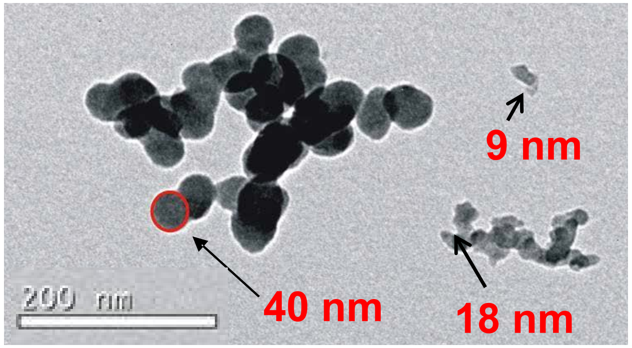
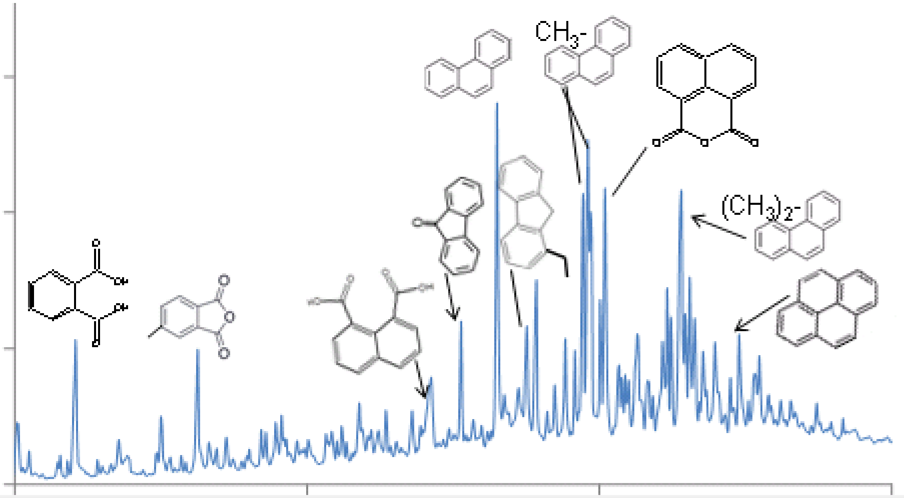
Fuel impacts on GDI particulate emissions

- With introduction of the efficiency gains of GDI technology, particulate emission in gasoline-fueled vehicles is a concern
- Understanding how fuel composition effects PM formation and its reactivity is important
  - Obvious reasons: regulation and public health
  - Less obvious reasons:
    - Mechanisms: e.g. “smoke-free” combustion that generates PM
    - Fueling: differences in strategy leading to different PM outcomes
    - Positive and negative fuel and lube effects

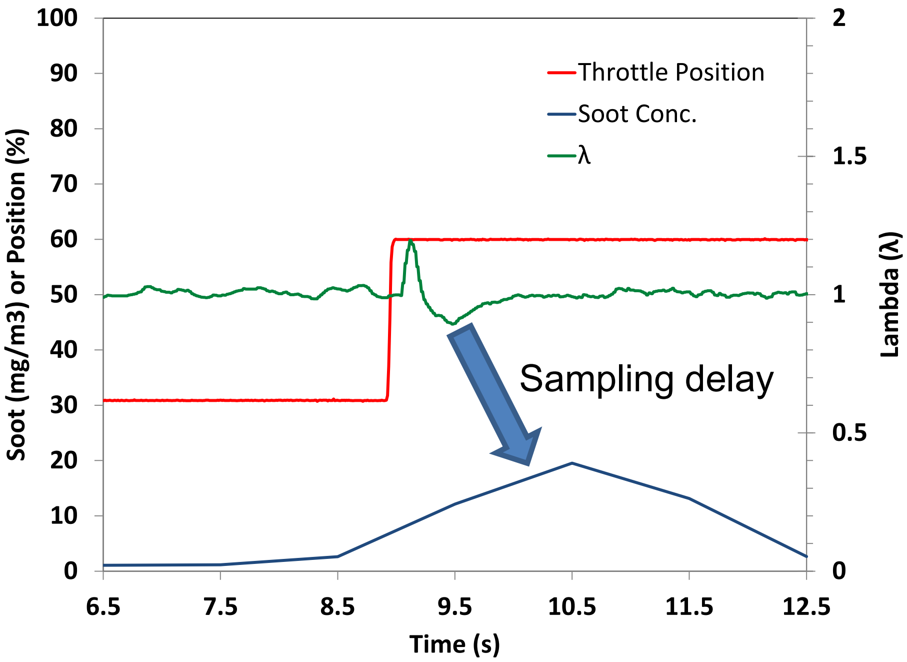


- History of distinctive PM diagnostics at ORNL-FEERC
  - Soot chemistry with pyrolysis GC-MS
  - Quantitative morphology assessment
  - Soot reactivity and oxidation kinetics
  - Many advanced platforms to study at ORNL
    - GDI, lean-GDI, RCCI, etc.



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

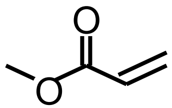
- GDI stoichiometric engine operated to mimic "tip-in" point of acceleration
  - novel approach designed to capture mode of maximum PM generation*
  - Brief period of rich operation (λ = 0.91) , medium-high load
- Specific focus on fuel oxygen effect on PM characteristics
  - E30, IB48; equivalent fuel 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

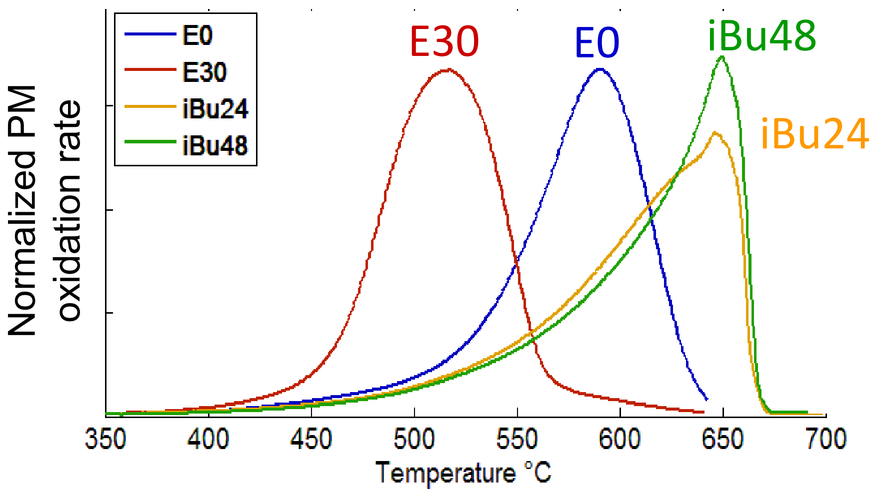
PM chemistry significantly affected by fuel-blend; EtOH increases reactivity, iBu decreases reactivity

- **Gasoline/Ethanol Blend: E30**
  - Highest PM reactivity
  - Unique oxygen containing compound observed in E30 PM

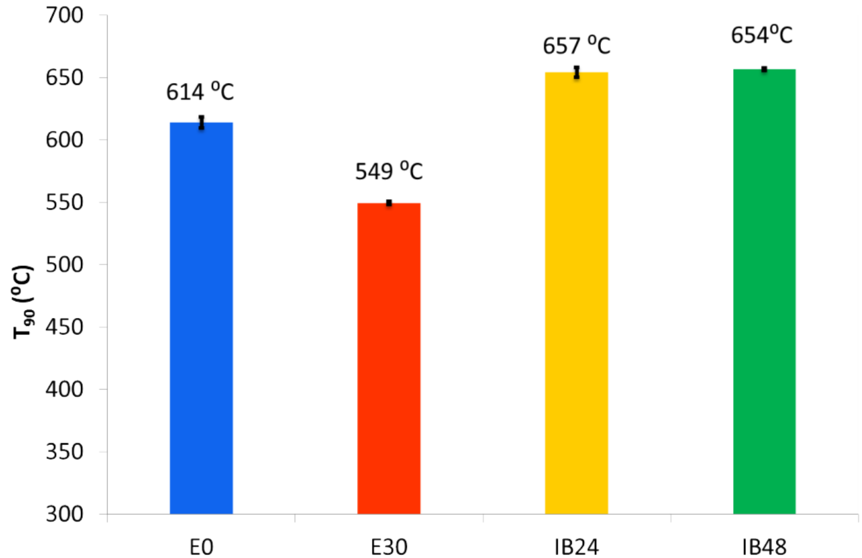


methyl propenoate

    - could facilitate auto-oxidation

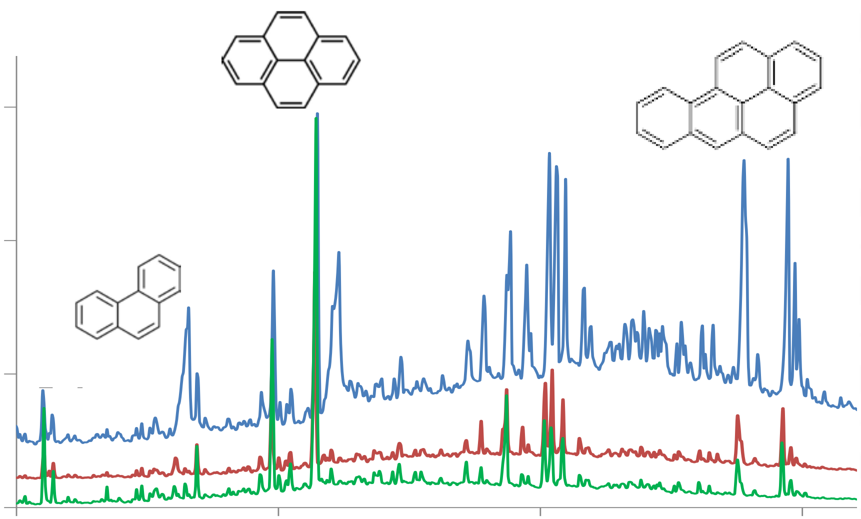


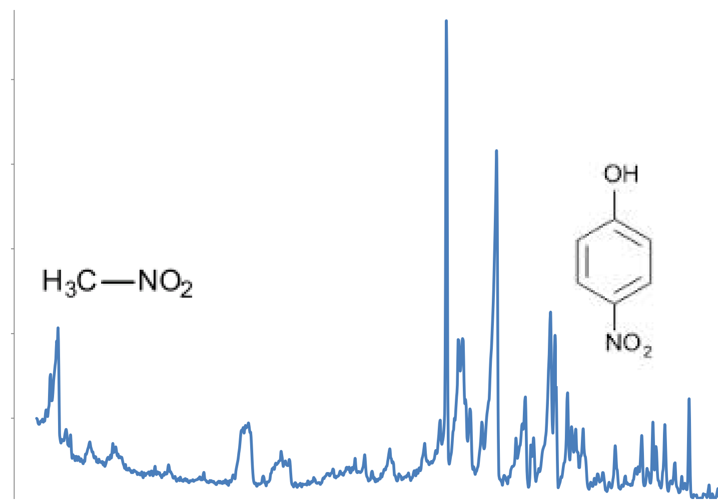
- **Gasoline/iso-Butanol: iBu24, iBu48**
  - Both blends have significantly lower reactivity than E0 or E30
    - Low temperature oxidation reactivity similar to E0
    - T90 is 40-43°C greater than E0
  - Soot oxidation temperature and profile similar for both iBu blend levels
  - Pyrene is predominant PAH present



Chemical Characterization to Enable New Fuels, Lubricants, and High-Efficiency Combustion

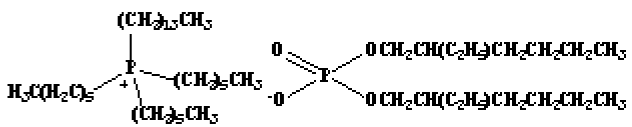
- Objective
  - New ways of sampling and measuring fuel, lube and exhaust species from new combustion regimes with alternative fuels
- Result: Biofuels can increase or decrease air toxics like PAH on PM
  - Developed size-resolved PM sampling method and direct thermal analysis method that avoids problems with solvent extraction and has much higher sensitivity
- Result: Nitrogen-based additive for RCCI operation with single fuel increases NOx post-DOC
  - Developed solid phase extraction sampling and identifying nitro-organics in the exhaust.
  - Nitro-organics poorly detected by HC and NOx analyzers observed in SAE 2014-01-1596





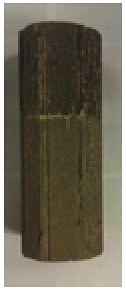
Lubricant-additive compatibility study with TWCs

- Collaboration with Jun Qu lubricant project on next generation lubricant additives using IONIC LIQUIDS (IL)*
  - GM and Lubrizol industrial partners
  - IL-18 additive demonstrated 2-4% increased fuel economy over Mobil-1
  - IL-18: $[P_{66614}][DEHP]$



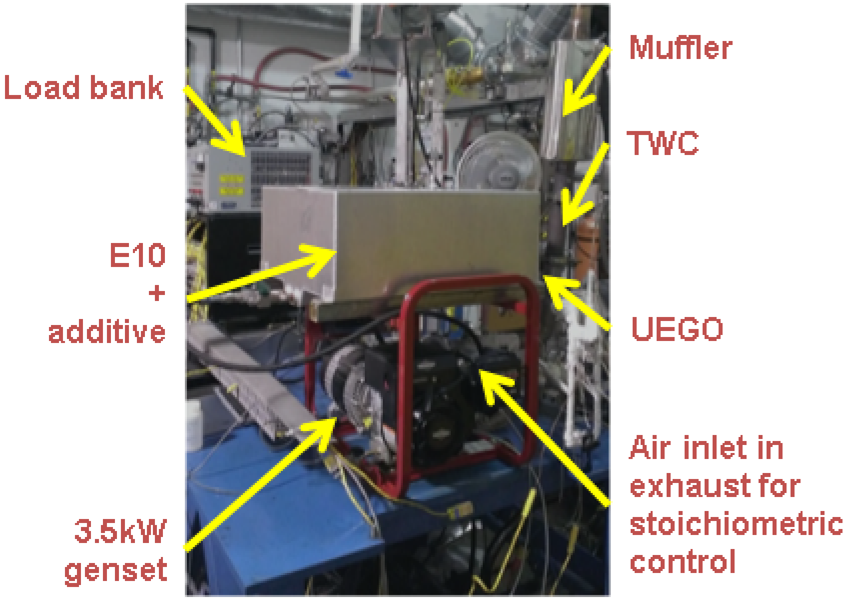
- **Is new additive compatible with current emissions control technology?**
  - Focus efforts on TWCs thermally-aged to full-useful life (FUL)
  - Use genset to introduce lifetime additive dose to FUL-TWC
    - Compare to industry-standard ZDDP and blank case (no additive)
  - Evaluate aged TWCs in flow reactor
  - Perform materials characterization to identify location/nature of P

Commercial TWC

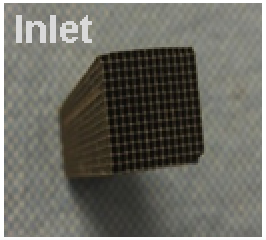


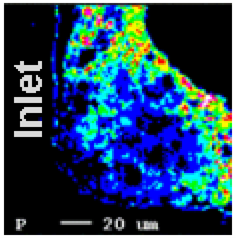
Catalyst core for engine aging

Lubricant exposure using gasoline genset



Aged TWC evaluation

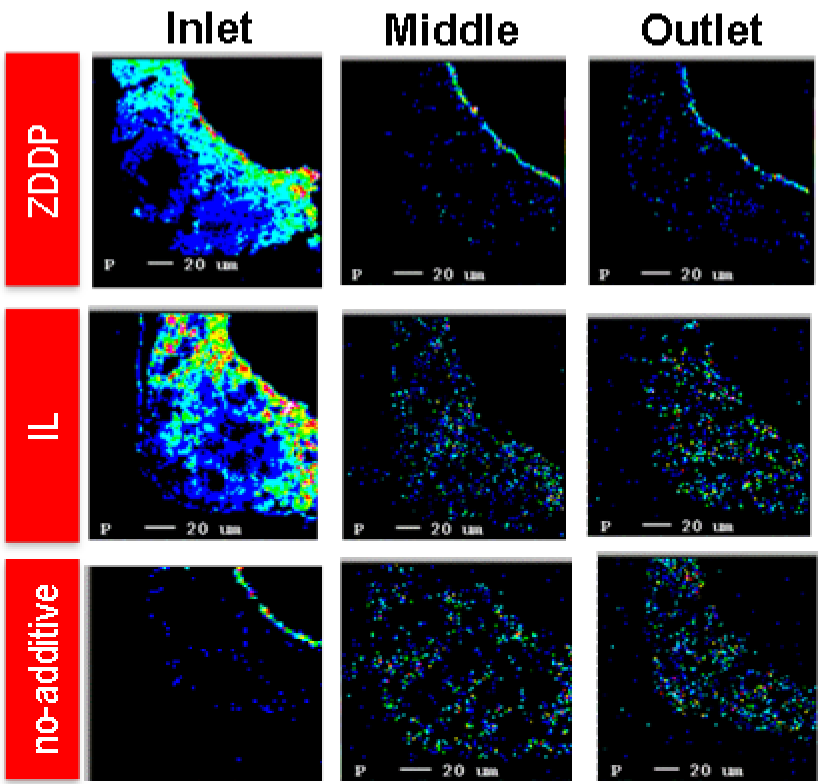




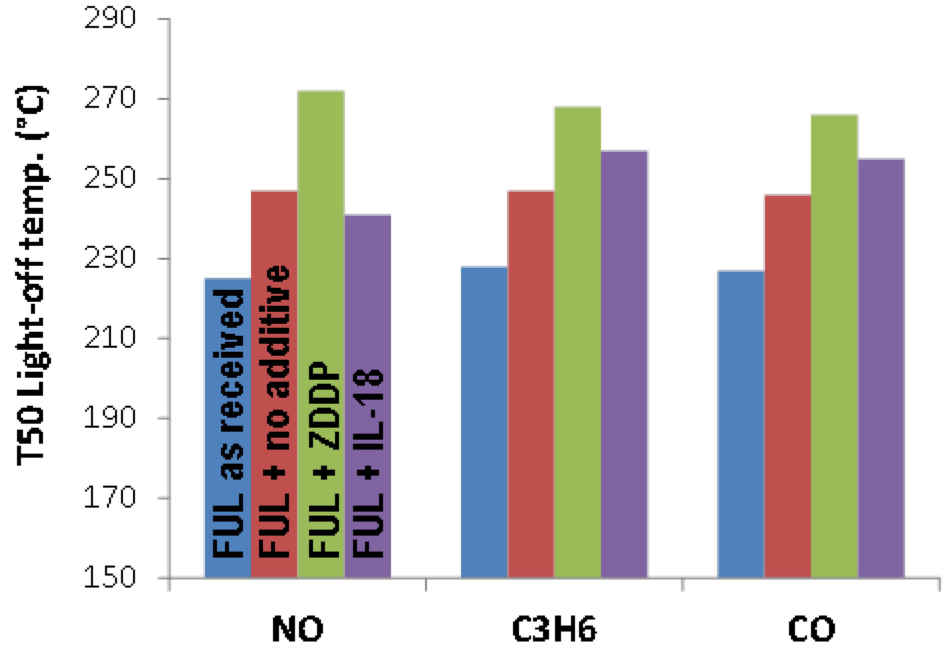
* - Jun Qu presentation in FT014 at 4:45 PM Thursday, June 19

IL has moderately less impact on TWC than ZDDP

- For the IL-18 aged TWCs the T50 for each probe gas is less than ZDDP-aged TWCs (FUL + ZDDP)
  - Measured for the inlet portion only



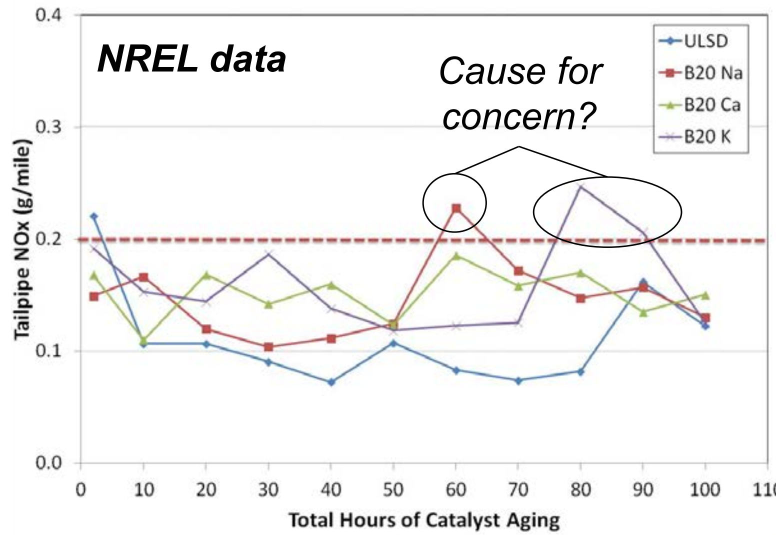
P content measured by EPMA



- Both ZDDP- and IL-aged TWCs show P saturating the entire washcoat
  - Temperature maintained at 900°C at inlet during exposure; net stoichiometric
- IL-aged TWC mimics no-additive at middle and outlet
- Exact form of P on TWC still being investigated

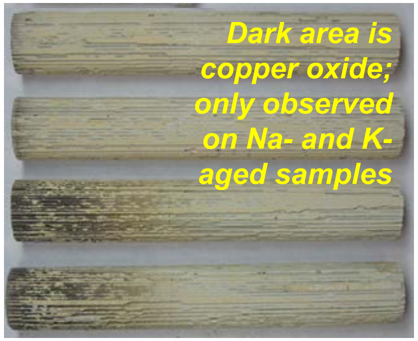
Compatibility of biodiesel with diesel emissions control devices; metal specification evaluation

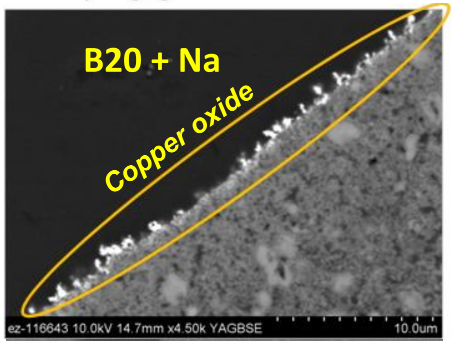
- **Are metal specifications for biodiesel sufficient for B20 compatibility with emissions control devices at end of full useful life?***
  – Na+K < 5 ppm   and   Ca+Mg < 5 ppm
  – Concluded they are adequate for most-light-duty applications
  – HOWEVER, important deactivation mechanism identified for consideration



- Need to conclusively answer impact on heavy-duty applications with longer durability requirements
  – 435,000 versus 150,000 miles

ULSD-Front
Ca-Front
Na-Front
K-Front



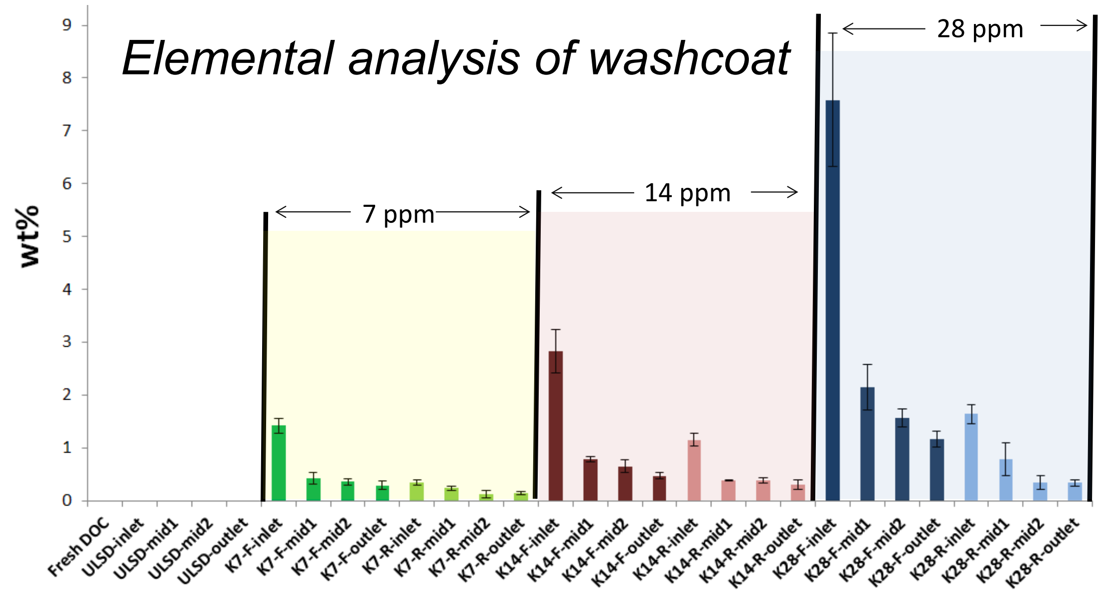


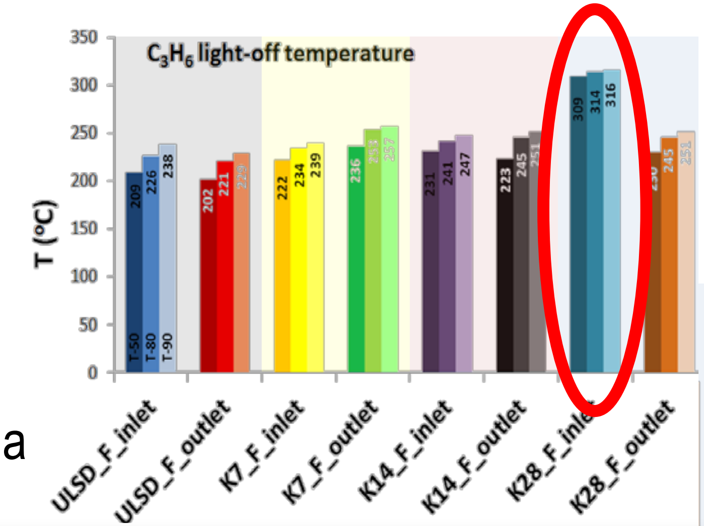
- Before starting long-term exposure need to understand limits of accelerated aging: **How high can the metal content be in the accelerated test before inducing unrealistic deactivation?**

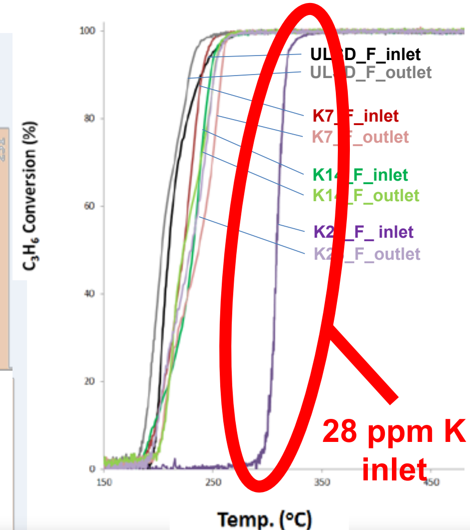
* - Collaboration with NREL (FT003) and DOE-Materials funded program (PM055)

For long term metal exposure studies, dosing above 14x falsely accelerates deactivation

- Exposed light-duty system to equivalent doses of K
  - 7 ppm → 200 h
  - 14 ppm → 100 h
  - 28 ppm → 50 h
- More K adsorbed on DOC with higher K concentrations, especially 28 ppm K
- Flow reactor evaluation also shows unbalanced deactivation
- 28x falsely accelerates aging
  - 14 ppm K similar to 7ppm K; justifiable
- 1000h heavy-duty durability exposure commenced with 14x Na
  - results reported next year







Remaining Challenges | Future Directions

- **Investigation of emissions control opportunities with biofuel blends**
  - *Unknown durability, engine platform effects, effects of other renewable fuels* → Sulfur and thermal exposure; engine evaluations started; butanol, super premium
- **Fuel and lubricant formulation impacts on GDI particulate emissions**
  - *Origins of PM in dual fuel combustion and GDI with renewable fuels* → Collection and analysis of non-soot PM; focus on fuel-rich portions of map
- **Assess Properties, Emissions, and Compatibility of Emerging Fuels and Lubricants**
  - *Quantifying/Identifying exhaust constituents resulting from renewable fuel combustion* → Fully integrate new thermal desorption pyrolysis GC-MS into research projects
- **Compatibility of ionic liquid lubricant (IL) additive with three-way catalysts (TWCs)**
  - *What is exact deactivation mechanism from IL? How is it different than ZDDP?* → Continue materials characterization to understand P interaction with TWC; new ILs
- **Compatibility of biodiesel with diesel emissions control devices**
  - *Is the metal content in biodiesel low enough for heavy-duty compatibility?* → Receive aged parts from NREL; evaluate performance and characterize materials

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:
  - Showed 95-100% NOx conversion with E50 and E85 in flow reactor; E85 better than E100
  - Designed novel approach to realistically capture mode of maximum PM generation
  - Determined PM chemistry significantly affected by fuel-blend
  - Developed size-resolved PM sampling method and direct thermal analysis method that avoids problems with solvent extraction and has much higher sensitivity
  - Demonstrated IL-based lubricant has moderately less impact on TWC reactivity than ZDDP
  - Determined acceleration factor of 14 x was justifiable for long term evaluation and that 28x falsely accelerates aging; 1000h heavy-duty durability exposure commenced
- Future Work: well-designed plans in place to address remaining barriers; guidance from industry incorporated into future directions

TECHNICAL BACKUP SLIDES

Investigation of emissions control opportunities with biofuel blends

Can broad inclusion of bio-derived alcohols in fuel 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:

- FY13: Demonstrated bench-scale NH_3 production for hybrid SCR designs and investigated its dependence on C:N ratio.
  - Showed 95-100% NO_X conversion over a broad temperature range
- FY14: Evaluated ethanol/gasoline in flow reactor
  - Showed 95-100% NO_X conversion with E50 and E85; E85 better than E100
- FY14: Established evaluation capability on lean gasoline engine platform

EtOH/gasoline blends

- Catalyst:
  - provided by Catalytic Solutions, Inc.
  - 2wt% Ag/Al_2O_3 washcoated on cordierite monolith
  - core sample: 2 cm D, 5 cm L
- Space velocity: 35000 h^{-1}
- Reductant:
  - blends of 200 proof EtOH and
  - EEE-Lube Cert Gasoline
- Fixed C/N

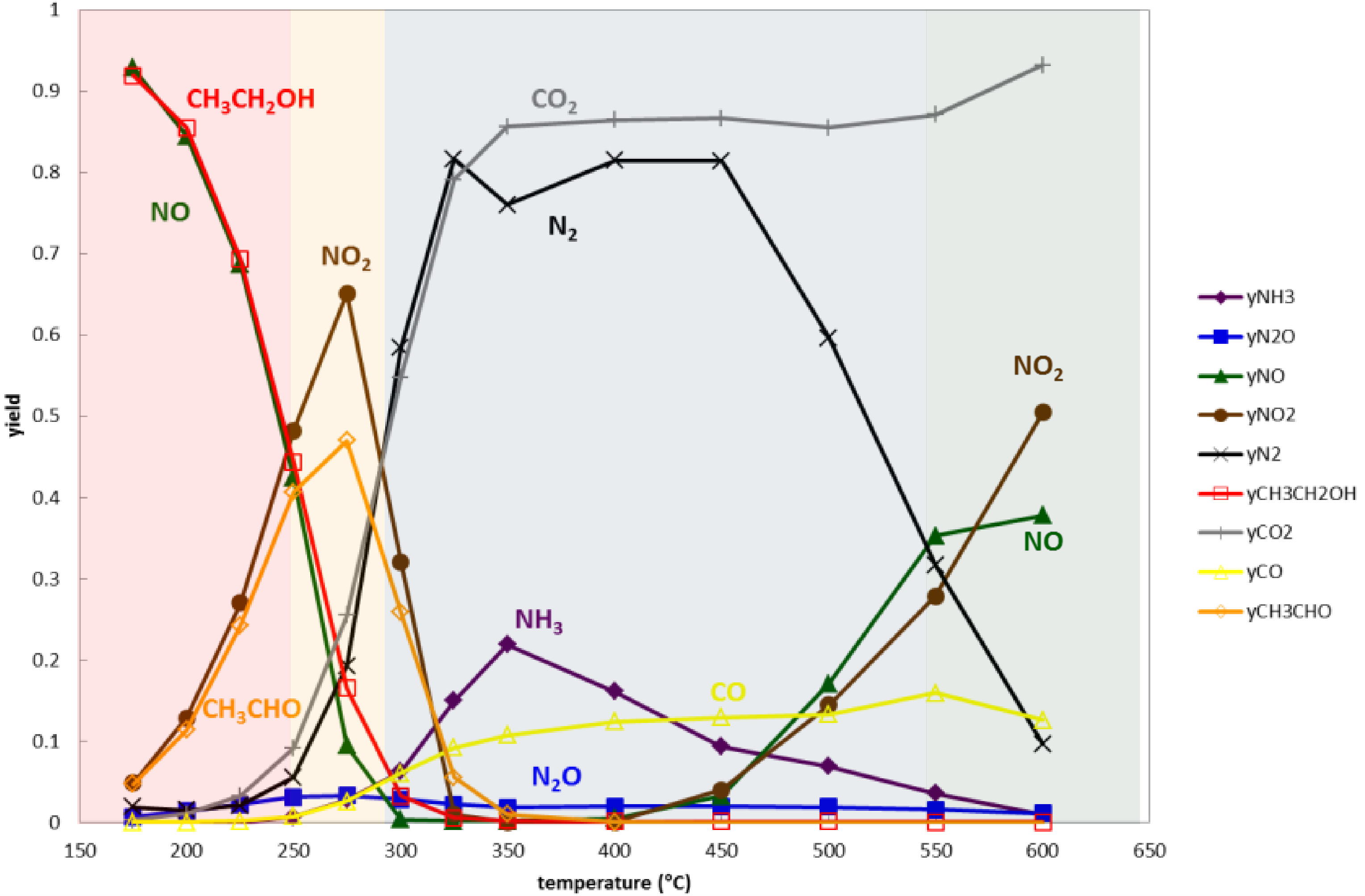
blend	EtOH (% v)	gasoline (% v)
E100	100	0
E85	85	15
E50	50	50
E15	15	85
E0	0	100

Gasoline properties		
C	wt %	86.5
H	wt %	13.5
O	wt %	<0.01
S	ppmw	4
aromatics	vol %	27.9
olefins	vol %	1.0
saturates	vol %	71.7
RON	--	97.0
MON	--	88.1

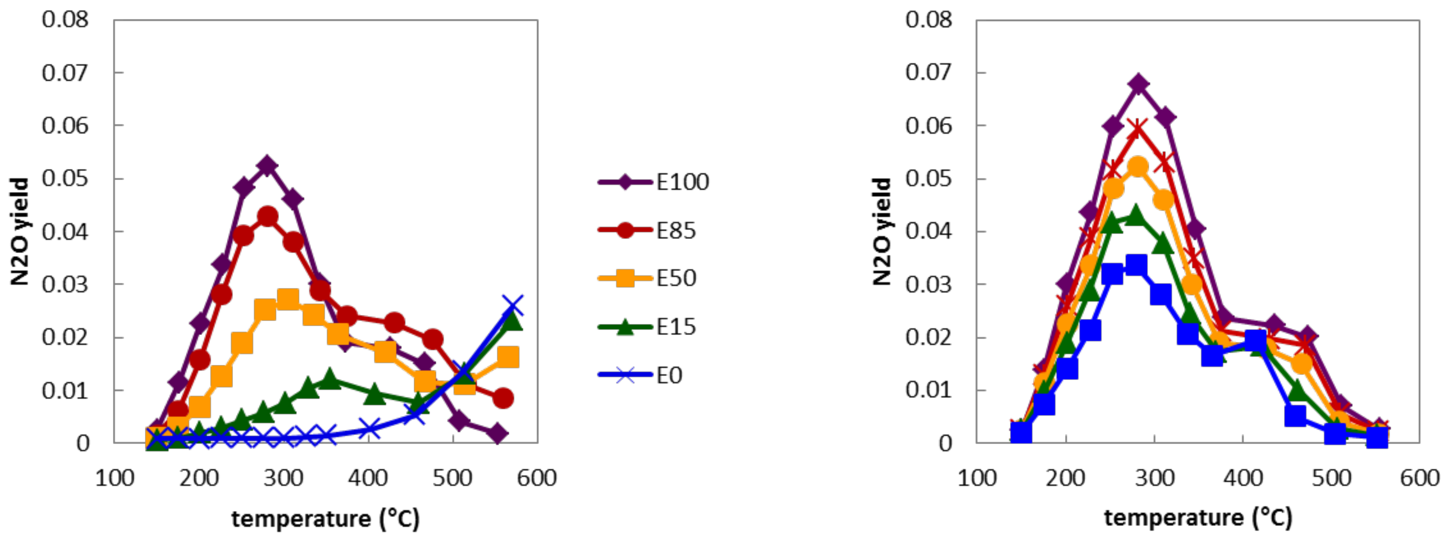
SV	(h^{-1})	35000
C/N	--	6
NO	(ppm)	500
O_2	(%)	10
H_2O	(%)	5

N- and C-based reactants/products show distinct temperature correlated relationships (E100)

- EtOH + NO → CH_3CHO + NO_2 → CO_2 (+ CO) + N_2 (+ NH_3) → CO_2 (+ CO) + NO + NO_2



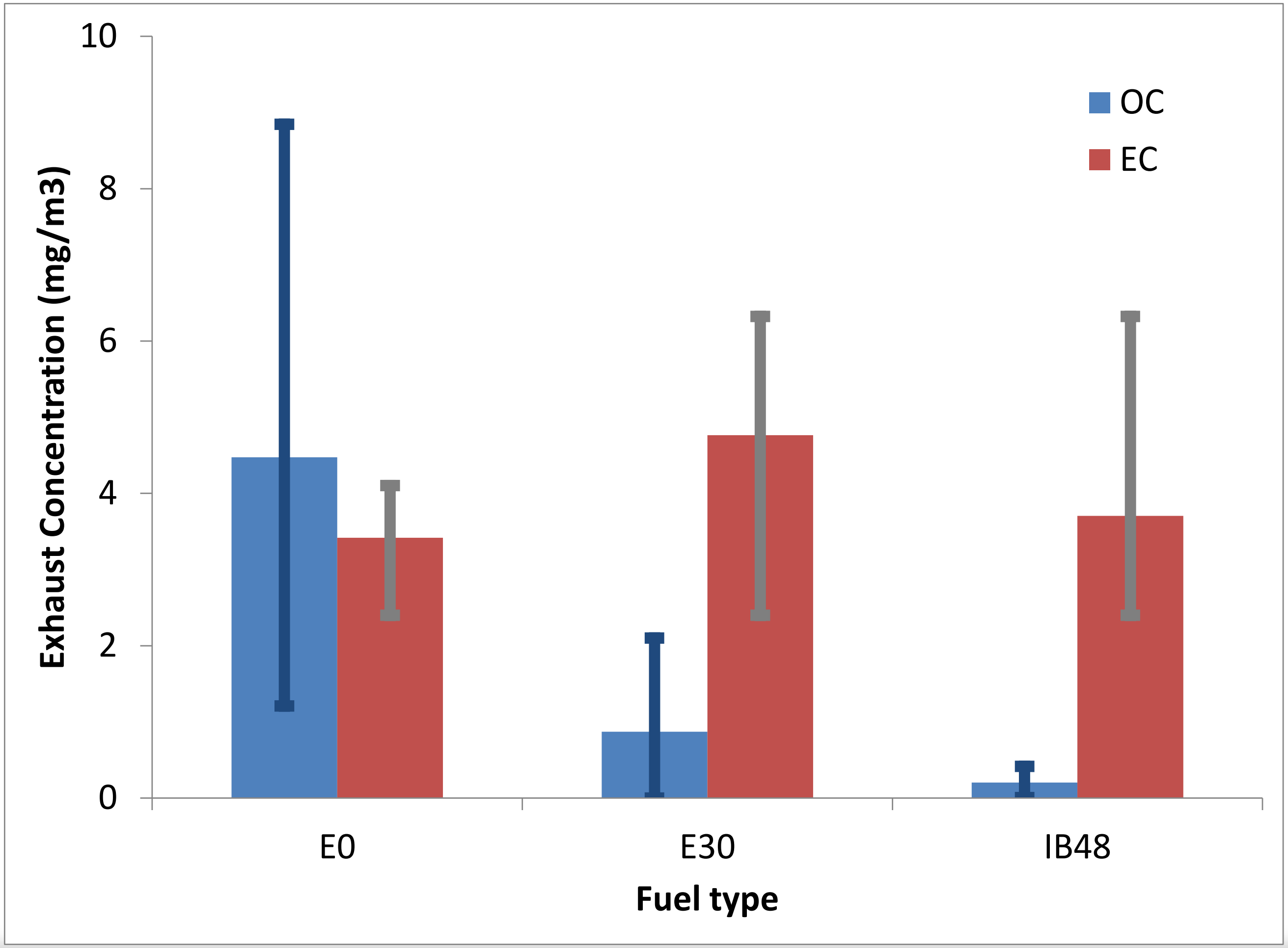
N_2O formation



- N_2O yield increases with:
  - EtOH content in blends with gasoline
  - C/N ratio for E100
- Peak N_2O production appears near lightoff for NOx conversion
- For these experiments, 7% yield corresponds to ~17 ppm N_2O

PM Fuels Project: Fuel effect on PM concentration

- Organic Carbon/Elemental Carbon showed some variability
  - Short sampling times lead to non-equilibrium conditions



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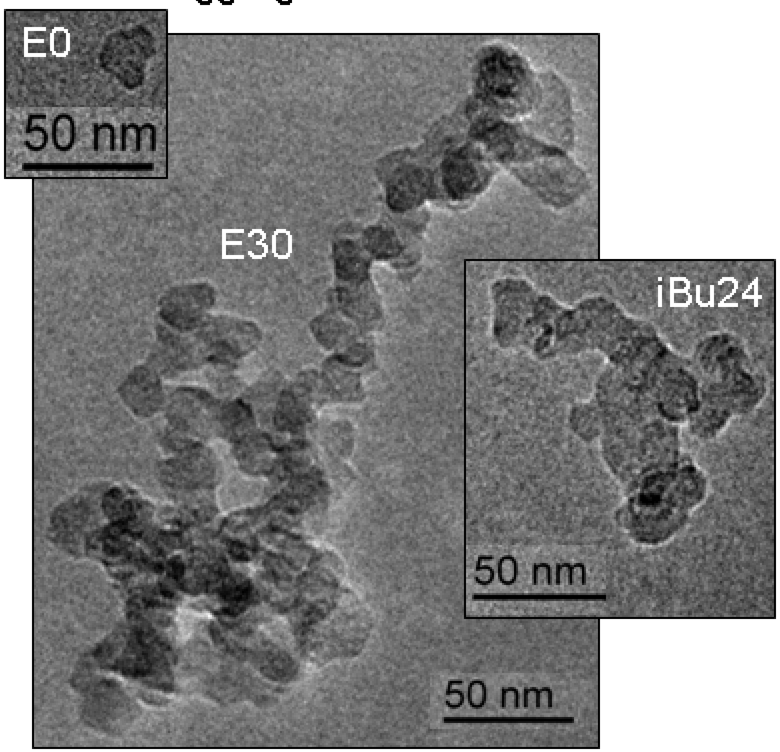
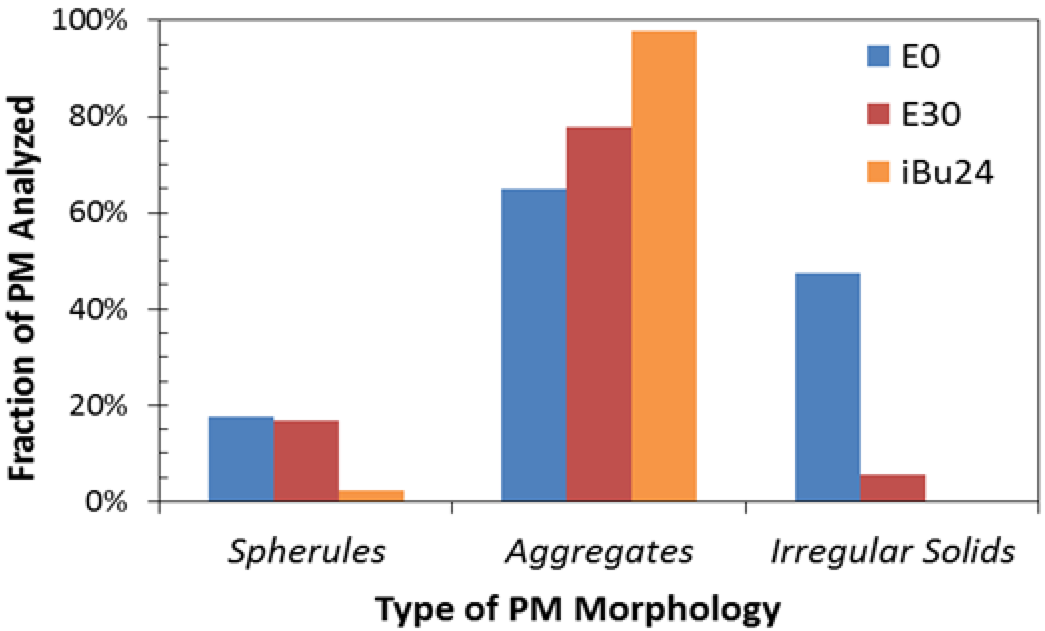
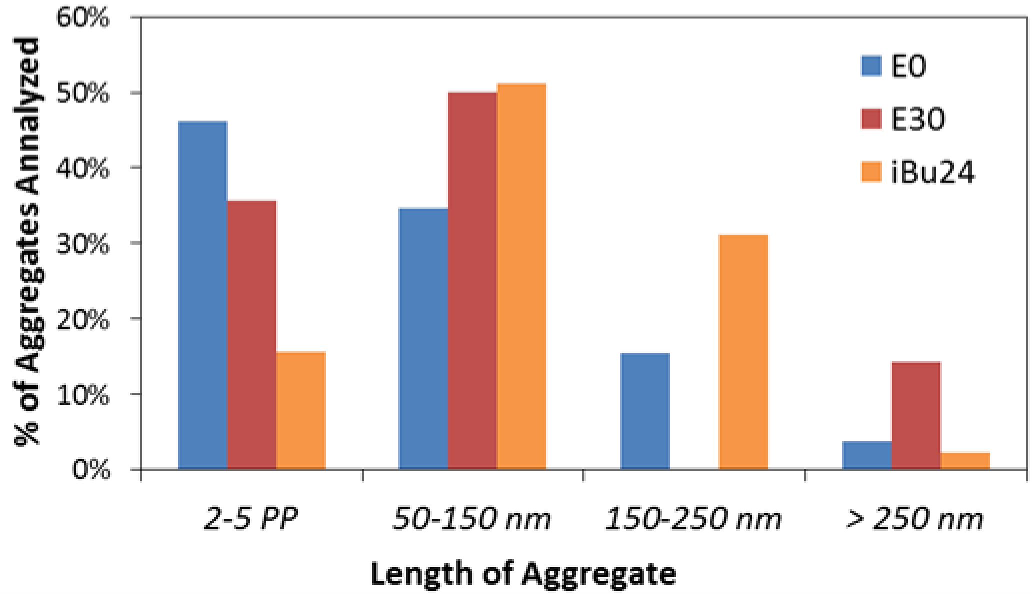
PM Fuels Project: Morphology

- iBu24 PM has uniform morphology type
  - Leads to larger aggregates
- iBu24 PM aggregates in narrow size distribution than E30
- E0 PM aggregates smaller

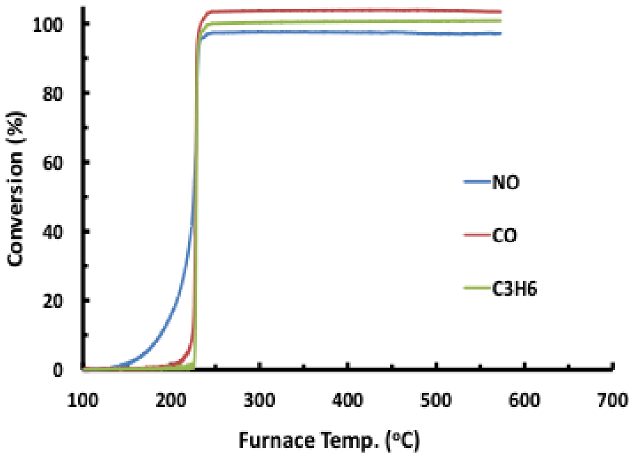




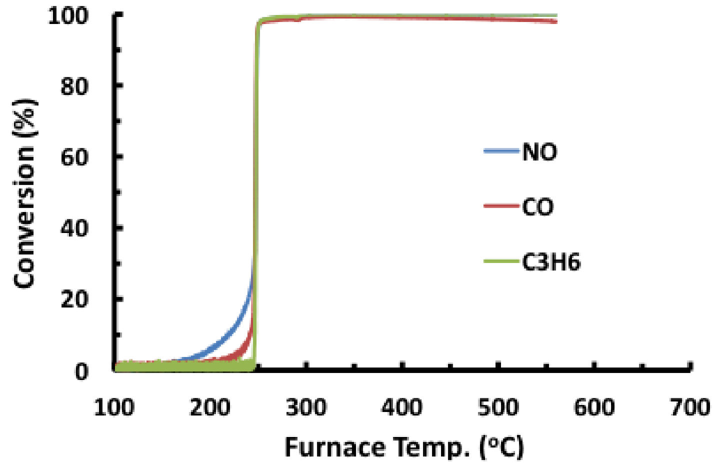


TWC inlet evaluated to measure impact of additives

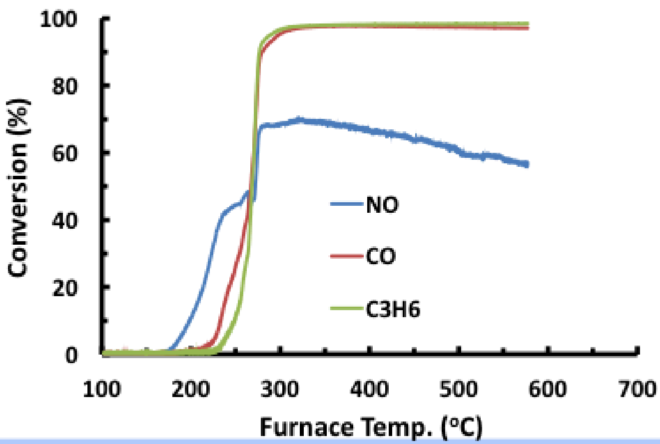
FUL



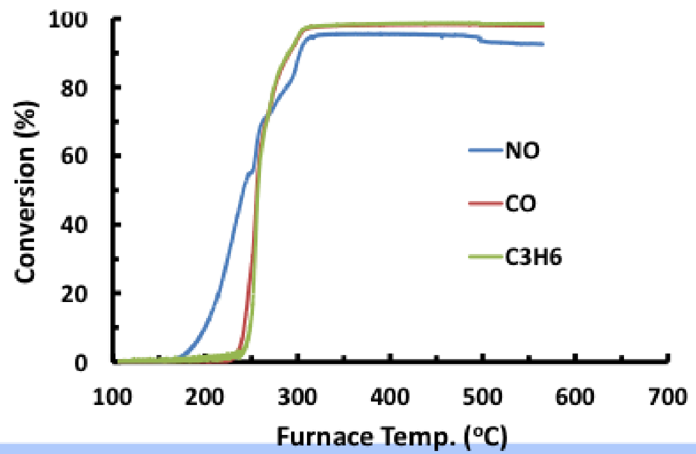
FUL + No additive (NA)



FUL + ZDDP



FUL + IL



- Difference between FUL+NA and FUL is minor for all 3 gases
- ZDDP-aged TWC shows the highest deactivation
- IL18 shows less impact than ZDDP