Impacts of Biodiesel on Emission Control Devices

Todd J. Toops and Bruce G. Bunting
Oak Ridge National Laboratory

D. William Brookshear and Ke Nguyen
University of Tennessee - Knoxville

DEER
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What impact could biodiesel have on emissions control devices?

- NaOH or KOH is a liquid-phase catalyst used in biodiesel synthesis
  - NaOH and KOH difficult to separate completely from products
  - Specification set at 5 ppm Na/K

- Anecdotal reports of accelerated ash accumulation with biodiesel use
  - Greater than 2 times faster ash accumulation observed at NREL

- Alkali absorption into monolith walls and possible weakening of monolith
  - K and Na would have similar impact

- Catalyst poisoning/fouling

Vegetable oil + methanol → NaOH or KOH

Increased Ash Accumulation

K migration into cordierite

Fresh

953°C
Biodiesel Impact on Emissions Control Devices

- Focusing on Na impact
  - Analyzing effects on all fronts
- Long term engine- and field-aged samples
  - Industry cooperation (GM samples)
  - NREL-aged samples
    SAE 2008-01-0080, SAE 2009-01-0281 & SAE 2009-01-1790
- Accelerated study using systems approach
  - Single cylinder engine; cycling to 650C
  - Artificially elevate levels of Na in B20
    - Accelerate aging
    - Levels elevated to achieve 435,000 mile Na exposure
- Characterization
  - Materials
  - Performance and kinetics
    - Bench reactor scale
LNT
Electron Probe Microanalysis (EPMA)

- Micrographs taken on each sample, with two micrographs being performed at separate locations on section 1
- Na, S, Ba, and S EPMA micrographs were obtained from each sample
- Elemental analysis achieved through line scans of image

Front | Rear
---|---
1 | 5
2 | 7mm
3 | 7mm
4 | 7mm
5 | 8mm
6 | 24mm
7 | 7mm
8 | 8mm
9 | 7mm
Cross-Sectional EPMA of LNT-1

- Five samples obtained from front NREL-aged LNT
  - Dual LNT system
  - Rear LNT not analyzed
- Na, S, Ba, and K EPMA micrographs were obtained from each sample
- Sulfur content is highest in first 10mm of front section
- Na layer on washcoat surface diminishes front to rear
  - Top 30 microns has up to 0.5%wt
LNT performance primarily affected by S

- Sulfur primary deactivation mechanism
- Performance recovered at 400 °C after bench desulfation (at 700 °C)
- Materials characterization suggests thermal effects impact performance at 200 and 300 °C
  - i.e., B20 is not suspected to impact LNT
  - Not surprising, Na will adsorb NOx

![Graph showing NOx conversion vs. evaluation temperature for Fresh, Field-Aged LNT-1, and Desulfated LNT-1](image-url)
Biodiesel and lube oil components found in DOC (GM-aged)

- S and P observed in DOC
  - S throughout washcoat at inlet of DOC
    - Average concentration
      - Inlet: 0.7%wt
      - Middle: 0.1%wt
      - Outlet: 0.03%wt
  - P at surface of washcoat
    - EPMA line scans
      - Maximum: 8%wt
      - Penetration: 30 μm

- Na observed at low levels
  - primarily in front section at washcoat surface
  - EPMA line scans
    - Maximum: 0.4%wt
    - Penetration: 30 μm
DOC minimally affected by aging

- Analysis of fresh, GM engine-aged and accelerated Na-aged DOCs

- Ethylene conversion minimally affected by aging
  - 88% → 80% at 250°C

- Oxidation of NO to NO₂ is slightly higher in aged DOC samples compared to fresh
  - May be due to small increase in PGM size
DPF
Ash in GM-aged DPFs – 20:1 for Ca:Na

EPMA of ash plugs in DPF

- Ash plugs apparent in rear of DPF
- 20x more Ca than Na detected in ash
  - Ca associated with standard lube oil
- Reported increase in ash accumulation may be due to:
  - Out of spec biodiesel, or
  - Increased oil consumption
- Little Na detected in wall of SiC DPF
EPMA micrographs at mid-section of accelerated Na-aged DPF (ORNL)

- High levels of S and Na present at mid-section of DPF
- Ash layer begins in middle and continues to outlet
- No significant Na penetration into cordierite DPF wall
  - DPF periodically regenerated at $T_{avg}=650 \, ^\circ C$
Na observed after accelerated aging in SCR, but not a surface-only effect

- Na throughout washcoat
  - In bulk ~0.2%wt
- Elevated Na levels also observed at surface
  - 0.3-0.6%wt
- Concentration of Na does not decrease significantly in the axial direction

- Low sulfur levels detected in SCR washcoat
  - Near detection limit
  - Increased level at surface ~0.1%wt
DOC→SCR→DPF system reveals impact in SCR performance with Na addition

- Single cylinder engine at constant load with high Na content
  - Periodic soot regeneration; $T_{avg} = 650$ °C
- Highly elevated Na-levels to achieve 435,000k mile equivalent Na (5 ppm basis)
  - 5000+ ppm Na and S in B20

- SCR performance measured on bench reactor with aged core

- NO-only performance evaluation is greatly impacted
  - When NO=NO$_2$ impact is minimal
  - Points to site specific deactivation
NH₃ interactions minimally impacted, but NO focused sites show deactivation

- No significant impact on NH₃ storage for the Na-aged sample
- NH₃ oxidation is inhibited above 400 °C in the accelerated Na-aged SCR...does not explain deactivation
- NH₃ adsorption sites are not impacted by Na

- Na contamination reduces the ability of SCR to oxidize NO into NO₂ over entire temperature range
- Combined with good conversions for NO+NO₂ feeds suggest: Na impacts Cu-exchanged sites
Summary

- Na identified in varying levels of emissions control devices
  - DOC and LNT at washcoat surface; SCR throughout
  - In DPF, Na is concentrated in ash plug

- Minimal impact observed on DOC and LNT devices

- Increased ash accumulation from using B20 is most likely due to either
  - Increased oil consumption brought on by oil dilution
    - Follow-up study coming

- Na does not migrate into the cordierite monolith
  - Thus no weakening of the monolith is currently suspected

- Na impacts zeolite based SCR catalyst
  - NO-only activity greatly reduced
  - NO₂=NO activity decreases moderately
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THANK YOU
Additional slides
System 1: Long-term NREL-aged LNT

- Part of long-term study at NREL to evaluate impact of B20
  - DOC → LNT-1 → LNT-2 → DPF
  - 120k miles aging equivalent (750h)
    - Operated at high loads to accelerate fuel consumption
  - < 0.5 ppm Na, K and 0.1 ppm Ca
- Only LNTs provided to ORNL for analysis
- Final state was before desulfation

System 2: DOC and DPF from GM

System 2: B20 $\rightarrow$ DOC $\rightarrow$ DPF

- Obtained from GM
- Field-aged system with B20
  - 120,000 mile equivalent
- No NOx aftertreatment in system
- Pt/Al$_2$O$_3$-based DOC
- SiC-based DPF
LNT-1 EPMA Line Scan

- Na penetration depth is approximately 30 microns and up to 1-3%wt locally
- S poisoning penetrates entire washcoat