Effect of Alternative Fuels on Soot Properties and Regeneration of Diesel Particulate Filters

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Sponsors:
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National Energy Technology Laboratory
Pennsylvania Department of Environmental Protection
Cummins Engine Company
Background

- Observations of a soot nanostructure-oxidative reactivity relationship, reported at DEER 2004, evidenced by lower regeneration temperature for biodiesel (B20) blends and greater oxidation rates in TGA/DSC measurements as well as in on-engine DPF regeneration tests – what is the source of this difference in PM regeneration process and how do these soots behave during oxidation?

- Vander Wal et al. published in *Combustion & Flame* in 2003 and 2004 papers demonstrating: (1) differences in the structure within soot primary particles with benzene, ethanol and acetylene, and (2) particles with less ordered structure provided higher oxidative reactivity
Objectives
Ultra Clean Fuels Project

- Determine the Interaction between Formulation of Conventional, Renewable and Synthetic Diesel Fuels and their Injection Characteristics
- Measure Physical Properties of Fuels that Can Provide Support for Understanding Injection, Combustion and Emissions Performance of Diesel Fuels
- Use Injection Studies, Physical Properties, Emissions Measurements and In-Cylinder Visualization to Determine Optimal Fuel Formulations
- Link Feedstock and Fuel Production Process to Physical Properties and, Thereby, Injection, Combustion and Emissions Performance - Characteristics of Soot from Different Fuels – Considering Neat Alternative Fuels, B100 and FT100
Research Strategy

- Feedstock
- Fuel Production
- Fuel Properties

Feedback of Behavior and Performance Information

- Fuel Properties
- Injection Characteristics

- Combustion
- Pollutant Formation

- Particulate Filtration
- DPF Regeneration
- NOx Reduction

- Spray Visualization Chamber
- Bulk Modulus of Compressibility

- AVL 513D Engine Videoscope
- Particulate and Gaseous Emissions

- Various Aftertreatment Strategies
Schematic diagram of the Cummins ISB test stand
Outline
Ultra Clean Transportation Fuels from Natural Gas

- Review of Key Observations Reported at DEER 2004
- Influence of Fuels, Injection Timing, Combustion and Emissions on the Performance of Aftertreatment Devices
  → Characteristics of Soot from Different Alternative Fuels
Fuel Composition Effects on Emissions
BP-325 and BP-325/B20 Test Fuels in a High Temp Regeneration

Regeneration Rate's Dependence on NO₂ produced

NO₂ produced (ppm)
0 50 100 150 200

Pressure Drop (mbar)
70 80 90 100 110 120

Time (min)
0 20 40 60 80 100 120

Equilibrium NO₂
Variation in Heavy Hydrocarbon Fraction

Soot Morphology

(c) BP15 Derived PM

(d) BP15B20 Derived PM
Initial Results – Comparing Diesel and B20

Soot Nanostructure – Less Ordered Nanostructure Corresponds to Enhanced Reactivity

(a) BP15 Derived PM
(b) BP15B20 Derived PM
Soot Nanostructure and Its Effect on Reactivity

Low temperature Reactivity from DSC/TGA test
- under 21% oxygen gas with treated samples

(a) Burning rate DSC curve
(b) Mass reduction TGA curve
Low Temperature Regeneration

BET Temperature to be lower by 30 °C with B100

30 °C shift of temperature where maximum NO₂ is produced over DPF
High Temperature Regeneration (from 280 to 450 °C)
Electron Microscopy of Initial Soot Nanostructure

(a) BP15 Derived PM

(b) BP15B20 Derived PM
Initial Soot Nanostructure

(c) B100 Derived PM

(d) F-T diesel Derived PM
From a comparison of DPF regeneration behavior:
- Enhanced regeneration of B100 in terms of both rate and BET is observed, whether this comes from particulate reactivity or catalyst activity which is sensitive to fuel sulfur.
- This difference in oxidation rate of DPF soot cake is reproduced in mass based rate on TGA as will be shown.
Raman Analysis of Initial Structure

<table>
<thead>
<tr>
<th>Graphitic order</th>
<th>Soot type</th>
<th>D band cm⁻¹</th>
<th>G band cm⁻¹</th>
<th>$I_d/I_g$ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>BP15</td>
<td>1354</td>
<td>1598</td>
<td>1.11</td>
</tr>
<tr>
<td>4</td>
<td>B20</td>
<td>1354</td>
<td>1598</td>
<td>1.18</td>
</tr>
<tr>
<td>1</td>
<td>B100</td>
<td>1354</td>
<td>1598</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>FT</td>
<td>1354</td>
<td>1598</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>1354</td>
<td>1583</td>
<td>0.37</td>
</tr>
</tbody>
</table>

*$I_d/I_g$ was extracted from 2 curves deconvoluted after lorentzian curve fitting.

Error bar: ±5% (± 0.05)
Raman Analysis of Initial Structure

(a) B100

(b) FT
XRD Analysis of Initial Structure

(c) BP15

(d) B20

![Images of samples](Image)

Bar chart showing the comparison of different samples with error bars.

Legend: BP15, B20, B100, FT, Soot

Graph showing the variation in metric $L_c / d_{002}$ with error bars.
Structural Change During Early Stage of Oxidation (30min)

FT

Initial

Oxidized

B100

FT

Int. (arb. unit)

1300 1400 1500 1600 1700
Raman Shift (cm⁻¹)

5% change

60% change
The Energy Institute

**Electron Energy Loss Spectra**

**% change of $I_{\pi}/I_{\sigma}$ ratio by EELS**

<table>
<thead>
<tr>
<th>Soots</th>
<th>Before</th>
<th>After</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>0.642</td>
<td>0.610</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>(±0.03)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B100</td>
<td>0.650</td>
<td>0.489</td>
<td>-26</td>
</tr>
<tr>
<td></td>
<td>(±0.03)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**% change to defect by Raman**

**% change of stacking order by XRD**
Surface Area Based Oxidation Rate

B100

Initial

Oxidized

Comparison of surface area and mass based oxidation rate

Remaining Question: Under surface burning, why did B100 soot undergo severe structural change even though its initial nanostructure was the same as for FT soot?
Oxygen Functionality of Initial Soot Samples

IR spectra band assignment

<table>
<thead>
<tr>
<th>Range (cm(^{-1}))</th>
<th>Chemical group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>Lactone, Carboxyl (bonded to two O or OH atoms)</td>
</tr>
<tr>
<td>1600</td>
<td>Aromatic C=C stretch C=O conjugated with aromatic</td>
</tr>
<tr>
<td>1450</td>
<td>Aliphatic C-H</td>
</tr>
<tr>
<td>1400</td>
<td>Sulfate</td>
</tr>
<tr>
<td>1250</td>
<td>Ether, Phenol</td>
</tr>
<tr>
<td>Below 1200</td>
<td>Electronic Noise due to high absorption of Kbr</td>
</tr>
</tbody>
</table>

From Fanning, Boehm, Smith
Summary

- From a comparison of particulate reactivity:
  - There is no definitive impact of initial nanostructure on oxidation rate
  - Under surface burning dominance during the early stage oxidation, the degree of internal structural change exerts a strong influence on the oxidation rate
  - The relative amount of initial oxygen groups is an important factor governing the soot oxidation rate
B100 Soot

105k x

75% burn off, 50 min

500k x

800k x
Fringe Length Analysis - B100 Soot

Initial

40% burnoff

75% burnoff

B100 soot-initial
Mean $L_a = 2.8 \text{ nm}$

B100 soot-ox30min
Mean $L_a = 1.3 \text{ nm}$

B100 soot-ox50min
Mean $L_a = 4.5 \text{ nm}$
The Energy Institute

Intensity (e-)

Energy Loss (eV)

Initial

75% burnoff

40% burnoff

Decrease in D band

Prominent graphitic peak

20% decrease

60% change

\[ \frac{I_x}{I_o} \]

0.786

0.489

0.650

Raman Shift (cm\(^{-1}\))

Intensity (e-)

Energy Loss (eV)
Oxidation Progression Model for B100 Soot

For simplicity, ignore crosslinking in this shell-core structure.

Once micro pore is fully penetrated, central hollow.

Further coalescence, due to physical factor such as increase in layer mobility and minimizing a strain energy.
FT Soot

105k x

75% burn off, 105 min

Still wavy and much shorter layer than B100
Fringe Length Analysis - FT100 Soot

Initial  20% burnoff  40% burnoff  75% burnoff

FT soot-initial
Mean $L_a = 2.8$ nm

FT soot-ox105min
Mean $L_a = 2.1$ nm

FT soot-ox30min
Mean $L_a = 2.3$ nm

FT soot-ox50min
Mean $L_a = 1.7$ nm
Gradual increase in D band and decrease in relative ratio of graphitic peak suggesting a tendency toward disordered state.
Comparison of Burning Regime

- Deviation from surface burning
- 10 to 1 Internal burning
- Surface Burning
- Abrupt oxygen consumption in B100

Graph showing the comparison of surface burning and internal burning with % Oxygen Content and Burn off (x) axes.
Summary

- B100 soot results in capsule type oxidation through internal burning, leading to a more ordered layer arrangement
- FT100 soot undergoes surface burning and less layer rearrangement than B100 soot, even at 75% burn off
- Early dramatic changes in inner structure and subsequent hollowing out of primary particles is a crucial factor in enhancing oxidation
- Surface reactivity involved in the early stage oxidation also seems to be responsible for a layer arrangement at later stage
Conclusions

- Generalized Transition from surface burning to internal burning/layer rearrangement at later stage of oxidation
- Enhancement of oxidation and its unique process with B100 soot
- Importance of surface oxygen groups for a faster oxidation and layer arrangement
Doug Smith, Kirk Miller, Etop Esen, Jim Rockwell, Rafael Espinoza, Keith Lawson and Ed Casey of ConocoPhillips

US DOE-National Energy Technology Laboratory

Edward Lyford-Pike, John Wright and Vinod Duggal of Cummins

Ken Voss and Joe Patchett of Engelhard Corporation

Howard Hess of Johnson-Matthey

Dr. Farley Fisher of the National Science Foundation for supporting the acquisition of the AVL Videoscope (Grant# CTS-0079073)

This presentation was prepared with partial support from the U.S. Department of Energy under Contract No. DE-FC26-01NT41098. The Government reserves for itself and others acting on its behalf a royalty-free, nonexclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit, and perform this copyrighted paper.

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