Impact of Biofuel Blending on Diesel Soot Characteristics



OF WISCON

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Motivation: Emissions effects of biodiesel fuels are of

growing concern

- Transesterified soy oil (SME) is most common biodiesel.
- Conventional diesel fuel (ULSD) has a broad hydrocarbon envelope C8-C22, centered at C18.
- SME biodiesel contains two long chain methyl esters, C16 and C18 (C25 equivalents).
- Chemical differences suggest that biodiesel soot is likely to be different, which would impact DPF regeneration and control.
- Critical need for DPF kinetic parameters for model accuracy and control strategies.





Diesel soot has two major components

- Elemental carbon (EC) forms the structural skeleton, just the EC portion without OC volatiles is referred to as char.
- Organic carbon (OC) is comprised of hydrocarbons physically or chemically adsorbed to the EC. EC+OC = nascent soot.
- OC comes from incompletely consumed fuel or entrained engine lube oil.
- The relative amounts of EC and OC vary with the fuel type and engine operating point. (Kweon & Foster SAE 2003, Storey & Lewis SAE 2004)
- Changes in EC/OC are likely to have an impact on soot oxidation.
- DPF models need to be able to handle soots from different fuel origins.



Research Objective: Determine effects of biodiesel on oxidation properties of diesel soot

- Quantify the relative amounts of the major constituents (EC, OC) and their detailed chemical composition
- Determine effect on microstructure.
- Correlate the EC and OC properties and characteristics with oxidation kinetics.

Benefit: Results directly relevant to performance and control of diesel particulate emissions

Approach: Integrate soot collection, sampling, & modeling with ongoing biodiesel engine studies



Experimental Setup: Engine soot generation followed by physical and chemical characterization



Global combustion measured by cylinder pressure is similar for ULSD, biofuels



Therefore, soot differences are probably related more to chemical intermediates rather than global combustion rate.



Solvent extracted samples show biodiesel soot OC contains more methyl esters, less paraffins







TEM reveals shifts in soot EC with bio-diesel

- •Graphitic and fullerenic distributions shift with bio-diesel level.
- •Open structure implies more access to edge site carbons.
- •Structure may explain active surface area, reactivity trends.

B100



ULSD and B100 show very different characteristic lamella lengths







Note: Fringe length histograms set to the same scale, B100 sets height, intermediate blends set width.

Blends show heterogeneous character, wider array of lengths than either pure fuel.

Soot oxidation kinetics measured in microreactor



- BET Surface Area
- O₂ Chemisorption (Active Surface Area)
- Isothermal rate measurements in pulsed mode.
- 2-stages:

- 1) Packed bed containing soot and ZrO₂ beads
- 2) Downstream oxidation catalyst to convert all HCs and CO to CO₂
- Effluent gases monitored by mass 11 spectrometer.



TPOs of ULSD and B100 nascent soots

Reactivity of blends increases with biodiesel level

T10 by Fuel Type



Reactivity increases with OC level, but is unaffected by OC composition







O2 chemisorption also correlates well with reactivity



- O₂ chemisorption on devolatilized soot shows B100 has 60% greater affinity for O₂ as compared to ULSD.
- O₂ chemisorption higher for B20 & B100 samples, but minimum for B5.
- Implies O_2 surface availability (θ) may be higher for high biodiesel blends.
- Hypothesis: TEM images and combustion measurements suggest that low EC surface availability for low biodiesel blends is related to a subtle shift in combustion pathways for small amounts of oxygenates added to fuel.

Dividing O_2 active surface area by BET surface area measurements show the same fraction of active sites for both ULSD and B100 soots.



The number of active sites is proportional to the total surface area.

LH surface coverage (θ) is constant for the soots, B100 just has a lot more surface area.

Isothermal, pulsed oxidation experiments measure kinetic parameters

- Experiments over a range of temperatures:
 - Soot char brought up to temperature under inert conditions.
 - Fast switching valve used to switch between oxidizing (10% O_2) and inert flow.
 - Pulse duration range 2s- 120s depending on temperature. Pulse width chosen to keep exotherm minimal.
 - Temperature range of interest is fuel dependent, chosen from TPOs.
 - ULSD: 450C-600C
 - B100: 375C-525C



Kinetic Parameter Determination: ULSD Soot

- Rate of mass depletion in DPF is dependent on oxidation kinetics.
- $r = -d[C_s]/dt = k^*[C]^a[O_2]^b$
 - From the literature (Yezerets, coal) b=0.61
 - [O₂] = constant in these experiments
 - 10% O_2 is in large excess for C sample
- Since [O₂]^b is constant, it can be lumped into the effective k term --> r = k[']*[C]^a
 - For each T experiment, plot ln[C] vs t, from plots, can determine k²
 - For all T experiments, plot ln(k') vs 1000/T to get E_A



Implications for DPF modeling:

- Soot oxidation kinetics are heavily impacted by biodiesel fueling.
- Light-off temperatures for both the nascent and devolatilized soot decrease with increasing volatile fraction level in the nascent soot.
- Higher biodiesel blend level (with the exception of B5) creates a more open and fragmented EC structure that has more surface area available for oxidation.
- > DPF soot reaction kinetics should include:
 - Reaction rate parameters that correlate with fuel type
 - Effect OC (volatiles) level, but not explicit compounds
 - Effect of specific available surface area (θ), as it is affected by biodiesel blend

Explicit kinetic expressions for biodiesel soot are under development.

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Questions?