EMISSIONS FROM ETHANOL – GASOLINE BLENDS: PHYSICAL & CHEMICAL CHARACTERIZATION OF SIDI PARTICULATES

Chethan K. Gaddam, Randy L. Vander Wal

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Acknowledgements:
(Project title: SIDI Fuel Neutral Particulate Study)
INTRODUCTION

- **SIDI engine deployment and particle emissions**
  - Fuel efficiency
  - Reduce CO₂ emissions
  - PN emissions

- **Gasoline exhaust particles**
  - Health effects – asthma, lung cancer, respiratory & cardiovascular diseases
  - Climate effects – scattering & absorbing light, cloud nuclei

- **Blending ethanol with gasoline**
  - Octane enhancement
  - EU promotes bio-fuel use (5.75% by 2010 and 10% by 2020)
  - Ethanol trade – increase 25 fold by 2020

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J. P. Szybist et al., 2011; D. D. Dutcher et al., 2011; J.M. Storey 2010
**MOTIVATION**

- OEMs want to anticipate future requirements
  - when filtration is required
  - Nature of regulations (EU, California ?)
- If particulate filtration is required
  - Clues to adaptation of DPF technology
  - Particulate size and shape
- Remove volatile content

- SIDI particle morphology
  - Mathis et al. (2004) – volatility of 20 nm dia. particles
**Nanostructure**
- It will control oxidation characteristics
- Convolved with soot surface chemistry

**Aggregate Morphology**
- Dictates surface area available for heterogeneous chemistry

**Aggregate Size**
- Affects light absorption and scattering properties of soot, important for radiative forcing calculations.
OBJECTIVES

▶ Systematic characterization of SIDI soot
  ▶ Particle size distribution
  ▶ Soot morphology
  ▶ Nanostructure
  ▶ Oxidative reactivity
  ▶ Chemical composition
OUTLINE

- Introduction
- Objectives
- Approach
- Experimental setup
- Results
- Summary & Implications
APPROACH

SIDI Particulates

Physical Characterization
- TEM
- TGA

Chemical Characterization
- FTIR-ATR
- XPS
Gasoline direct injected Ricardo Hydra

- Single cylinder research engine
- Four-stroke engine

### Engine Parameter

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<th>Engine Parameter</th>
<th>Units</th>
<th>Value</th>
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<tr>
<td>Bore</td>
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<td>Stroke</td>
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<td>Displacement</td>
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<td>Clearance Volume</td>
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<td>Connection Rod Length</td>
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EXPERIMENTAL SETUP
3 fuels tested

- EPA Tier II EEE
- E20 (denatured ethanol:EEE, 20%:80% by volume)
- E85 (denatured ethanol:EEE, 85%:15% by volume)

### Engine Operating Conditions

> PM sampling was pre-planned

> Wide range of operating conditions with changes to A/F ratio, Load, Injection timing

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<td>Late EOI</td>
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</table>
Results

Physical Characterization
AGGREGATE MORPHOLOGY

- EEE and E20 – open, branched
- E85 – dense, compact
- Growth after aggregation for E85
AGGREGATE MORPHOLOGY

- Denser, compact
  - nucleation density
  - rate of concurrent/subsequent surface mass growth

- Significant variation in primary particle size within aggregate

[Images of aggregate morphologies at different loads and densities]
Mean particle size ~14 – 51 nm
  - Diesel soot ~19 – 35 nm

Primary particle size
  - Strong variation with fuel blend

Lee et al., 2002; Wentzel et al., 2003; Park et al., 2004; Zhu et al., 2005; Neer and Koylu, 2006; Barone et al., 2011
**Fractal Dimension**

- Aggregate – fractal like structures
- Irregularity – fractal dimension, $D_f$
- Power law relationship $n_{po} = K_f \left( \frac{d_g}{d_{po}} \right)^{D_f}$

Nanostructure – graphene layer plane dimensions, their tortuosity and relative orientation

Nanostructure was generally amorphous or lacked significant order.
Nanostructure is mostly amorphous & non-structured

Across test conditions for given fuel, nanostructure largely unvarying, *with one exception*
EOI 280 Condition

Vander Wal et al., 2003; Kuen et al., 2011
EOI 280 Condition

- Strong variation as evidenced by tortuosity distributions
- E85: More tortuosity – indicative of high curvature
- Implications of fuel oxygen content:
  a) soot forming processes might be delayed
  b) chemistry of soot formation is altered
  c) overall soot production is lessened
**PARTIAL OXIDATION**

- First [known] observation for soot oxidation from a Gasoline engine
- Evidence of oxidation – induced structural change
- HRTEM and fringe analysis repeated after partial oxidation of EOI 280 sample (E85 fuel)

E85 – EOI 280

E85 – EOI 280 – after oxidation at 550 °C
COMPARATIVE FRINGE ANALYSIS

Distinct change in nanostructure during oxidation

- Lamella become more longer, flattened
Results

Chemical Characterization
**MOTIVATION**

- SPLAT II – significant organic content (40%)
- Two VPR methods
  - Thermodenuder & Evaporative chamber
  - No difference
- Spectroscopy Tech.
  - XPS (Surface..)
  - FTIR-ATR (Bulk..)
Substantial organic content
Consistent with TEM results
FTIR-ATR Analysis

- Significant volume-averaged organic content
- Variation with condition – suggests different chemistries
  - More variation as a function of engine operation
  - Even within a single aggregate
- C-H (aliphatic) – more profound in Fuel-rich conditions
SUMMARY & IMPLICATIONS

- **Primary Particle Analyses**
  - Variation of primary particle size as a function of condition, fuel

- **Aggregate Morphology**
  - Fuel rich conditions: aggregates that are more compact
  - E85: high fusion between particles

- **HRTEM & Fringe Analyses**
  - General lack of structure, across range of conditions & fuel blends

- **Partial Oxidation**
  - Distinct change in nanostructure during oxidation
  - Lamella become more longer, flatter

- **FTIR – ATR Analyses**
  - Indicates significant matrix-distributed organic content
  - Fuel rich conditions led to soots with higher organic content
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