Investigating the Effect of Varying Ethanol and Aromatic Fuel Blends on Secondary Organic Aerosol (SOA) Forming Potential for a FFV-GDI Vehicle

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Secondary Aerosol (SA)

- SA has been measured to contribute up to ~ 75% of PM$_{2.5}$ in anthropogenic regions (Huang, et al. 2014)
  - Inorganic salts & Secondary Organic Aerosol (SOA)
- Inorganic salt formation in the atmosphere is well understood

\[ \text{NO}_x + \text{SO}_x \xrightarrow{\text{oxidation} \ (\text{OH, } O_3, \text{NO}_3)} \text{HNO}_3 + \text{NH}_3 \]
\[ \text{H}_2\text{SO}_4 + \text{NH}_3 \]

- Organic Aerosol, 20%-90% of submicron particulate mass, is less understood (Jimenez, et al, 2009)
  - Primary OA, primarily combustion of fossil fuels, and biomass burning
  - Secondary OA, is formed through the reaction of volatile organic compounds
- Gasoline powered motor vehicles have been credited to the majority of SOA mass in large cities (Bahreini, et al, 2012)
Ethanol Fuel Effects

- Reduction in various gaseous emissions
  - Variable THC and NMHC
- Lower tailpipe particle mass concentration
- Reduction in aromatic content
  - May directly decrease overall SOA potential of vehicles
- Previous work utilizing flow tube reactor displayed decreasing SOA formation from increasing ethanol fuel blends (Timonen, et al, 2016)

(Timonen, et al, 2016)

(C. Giametta, 2006)
UCR’s Mobile Atmospheric Chamber (MACH)

- Current mobile chambers restricted to a smaller volume (Platt et al. 2013, Presto et al. 2011)
- Low surface to volume ratio of 2.2:1
  - Minimize background effects (zero air/non-reactive chamber material/leaks) and wall losses (Aerosols/Semi-volatile aerosol precursors)

~30m$^3$ Volume makes it the largest mobile chamber

- UV lights are a substitute for sunlight
  - Peak UV=365nm

- Anodized aluminum sheets - 4250E Super UltraBrite 95, ACA Corp.

- Aerosol and Gas Phase Characterization
  - Aerosol: Size, Number, Density, Volatility, Hygroscopicity, Black Carbon
  - Gas: NOx, CO, CO$_2$, H$_2$O, and O$_3$
    - GC-FID, SIFT

Single collapsible ~30m$^3$ 2 mil FEP fluoropolymer film reactor (Saint Gobain)
Vehicle Used For Study

<table>
<thead>
<tr>
<th>Make &amp; Model</th>
<th>Engine</th>
<th>Mileage</th>
</tr>
</thead>
<tbody>
<tr>
<td>2017 Chevy Equinox</td>
<td>2.4L FFV</td>
<td>20,308</td>
</tr>
</tbody>
</table>

Each fuel was tested over a **cold** and **hot** start LA-92 Driving Cycle in triplicate

Dilution for all tests was ~185:1
Results

*All composition data was measured with an HR-ToF AMS*

- 75-90% of PM was BC
- Decreased PM emissions in hot start (average of 50% reduction)
- Highest emissions from the **HA E10** (10.26 mg/mi)

PM was strongly affected by both **ethanol** and aromatic content
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- 65% decrease in PM comparing LA E10 vs E30 (23%, 21% Aromatic V.)
- E78 displayed the least amount of PM with 0.49 mg/mi

75-90% of PM was BC

Decreased PM emissions in hot start (average of 50% reduction)

Highest emissions from the HA E10 (10.26 mg/mi)
Results

After the irradiation experiment, a negligible amount of secondary aerosol was formed all fuels. The two E10 fuels formed a small amount of SOA in the hot start. The vehicle exhaust when introduced to an “ultra clean” environment does not form secondary aerosol.
Surrogate Purpose

- Surrogate is a mixture of reactive organic gases (ROG) developed to mimic an urban area.
- Emission data was lumped into categories by reactivity.
- **Surrogate’s purpose is to provide a baseline reactivity**
- Within each category, species were weighted by reactivity and abundance in the atmosphere.
- Surrogate on its own forms no appreciable secondary aerosol mass.
- This is more consistent with what would occur when vehicle exhaust is emitted in urban areas.
This is the surrogate that was used for the remaining chamber experiments.

All procedures were the same as summarized earlier, with the addition of 1 ppmC of the surrogate, and ~45 ppb NOx.
Results after irradiation displayed the formation of a large amount of Ammonium Nitrate

For all fuels excluding E30, less secondary aerosol formed in the hot start experiments
Vehicle emitted an average of 2.9 & 2.1 mg/mi of NO\textsubscript{x} for cold and hot starts respectively.

- Resulted in only ~5-10 ppb NO\textsubscript{x} in chamber

NO\textsubscript{x} concentrations in surrogate experiments were 45-60 ppb

Similar NH\textsubscript{3} concentrations in both
Increasing aromatic results in increasing carbonaceous aerosol.

Increasing ethanol results in a decreasing carbonaceous aerosol.

Hot & Cold starts have different trends.
Largest amount of SOA formed with the **cold start** HA E10 (3.36 mg/mi)

**LA E10 hot start** formed the least amount of SOA (low THC emissions)

Overall there was a strong trend relating the SOA formed to the THC emitted

Both hot & cold starts fall on similar trendline

May allow prediction of SOA potential
Conclusions

- Average of 50% reduction in tailpipe PM in **hot** start
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  - Consistent reactivity & increased NOx
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  - Increased with increased aromatic
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  - Different trends with varying driving conditions
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- Total Carbonaceous (BC, POA, and SOA)
  - **Increased** with **increased aromatic**
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  - Different trends with varying driving conditions
- SOA formation vs THC trend
  - least reliant on driving condition
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