Gasoline Aromatic and Oxygen Content Impact Formation of Secondary Aerosols from a Gasoline Direct Injection Vehicle

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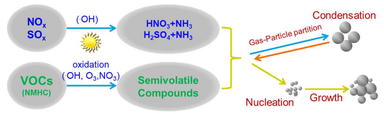
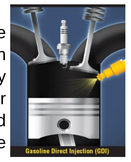
Background & Motivation:



Secondary Aerosol (SA) has been measured to contribute up to ~75% of total $PM_{2.5}$ in anthropogenic regions (Huang, 2014). Total SA consists of inorganic salts and secondary organic aerosol (SOA). Inorganic salt formation is well understood, and can be accurately modeled if emission inventories are accurate and up to date. Organic aerosol formation is much more complex and less understood. SOA is formed through the photo-oxidation of volatile organic compounds and in urban areas, gasoline powered vehicles are major contributors.



Driven by stringent legislative measures on vehicle GHG emissions, the transportation sector has changed significantly in the past decade with the introduction of gasoline direct injection (GDI) engines. In GDI engines, liquid fuel is sprayed directly into the combustion chamber allowing a higher compression ratio thus greater efficiency. Imperfect mixing due to incomplete fuel evaporation, results in increased soot emission for GDI engines (Karavalakis, 2015; Liang, 2013). The effect of the market shift to GDI engines on total secondary aerosol has not been fully explored.

Another variable that may affect the SA formation potential of emissions, is the composition of the fuel used. Currently conventional gasoline has 10% ethanol content but it has been found that higher ethanol blends could possibly lead to greater fuel efficiencies and lower greenhouse gas emissions (EESI, 2015). A fundamental issue linked with high ethanol content in fuel, is the increased production of ozone, acetaldehyde, and peroxyacyl nitrates (PAN) (Correa, S.M), however, the effect on SA formation is not currently understood.

Chamber, Vehicles, Fuels, & Testing Procedure:

UCR's MACh1 was used for irradiation experiments

- 30 m^3 2mil FEP Teflon film reactor (largest mobile chamber in the known universe)

Vehicle was tested over duplicate cold-start LA-92 driving cycles on 8 fuels

Figure 1: Mobile Atmospheric Chamber (MACh)

Make & Model	Emission Std.	Engine	Mileage
2017 Ford Fusion	SULEV	GDI, 1.5L Turbo Charged	24,491

#	EtOH Content (% vol)	Aro Content (% vol)	C10+ Aromatics	PMI
Fuel 1	0.0	21.2	4.456	1.748
Fuel 3	10.0	21.4	4.541	1.888
Fuel 5	14.7	20.3	4.36	1.722
Fuel 6	14.8	21.8	4.734	1.765
Fuel 8	19.6	19.1	4.112	1.613
Fuel 2	0.0	29.4	6.734	2.330
Fuel 4	9.6	29.1	6.157	2.152
Fuel 7	14.7	29.3	5.996	2.093

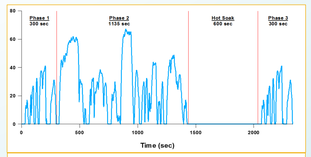
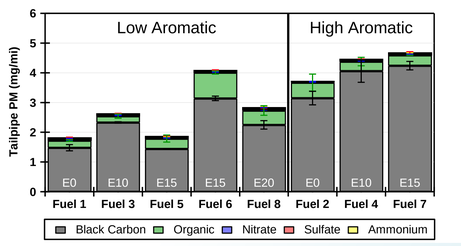
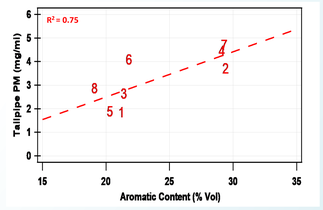


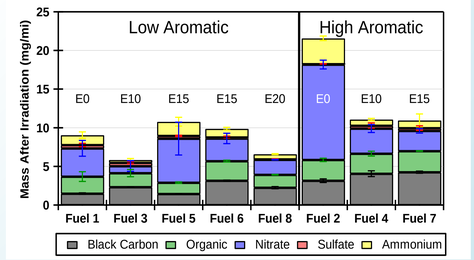
Figure 2: LA-92 Driving Cycle

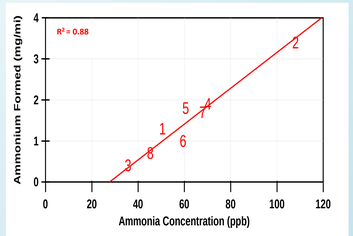
- Exhaust was introduced to the chamber throughout the entire LA92 driving cycle (excluding hot soak)
- 1.0 ppm of H_2O_2 was injected as the initial OH radical source

Exhaust Tailpipe & Aged Emissions Results:



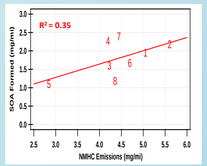


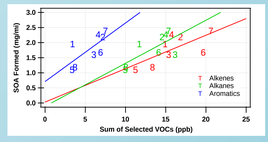




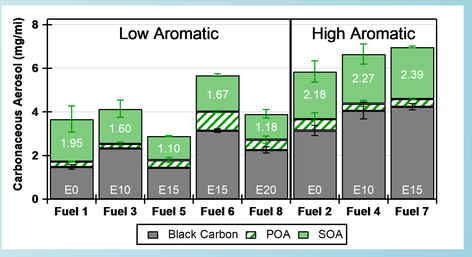
- 75-90% of PM was BC
- High aromatic fuels emitted larger tailpipe mass
  - 4.27 ± 0.82 mg/mi vs 2.65 ± 0.82 mg/mi
  - Fuel 6 averaged 4.07 mg/mi
- Fuel content affected fractional composition
  - LA BC content: 80.4% ± 4.3%
  - HA BC content: 89.2% ± 2.6%
  - No trend when comparing EtOH
- PM was strongly affected by aromatic content
- PM did not appear to correlate to ethanol content
  - Increasing trend with ethanol content observed when fuels split by aromatic content
- After the irradiation experiment, varying SA formed
  - 2.2-5.9 times increase
  - Largest total masses were all HA fuels
  - Largest was F2 HA
- Ammonium Nitrate (AN) had the largest contribution to total mass formation
  - $NH_3 + HNO_3 \rightarrow NH_4NO_3$
- Looked into correlations with NOx and NH_3
  - No real correlation with NOx
  - Strong linear correlation with NH_3
- Indicates NH_3 is limiting reagent in ammonium nitrate formation

- NMHC emissions and selected VOCs (precursors to SOA) show quite strong correlations with SOA
  - As VOC speciation is more specific, the linear correlation increases

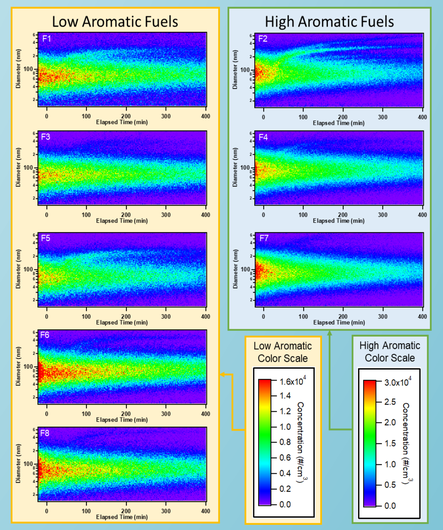




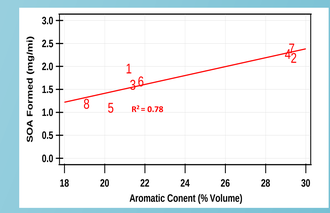
SOA Formation & Fuel Composition Effects:

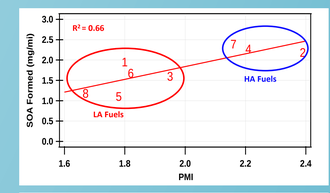


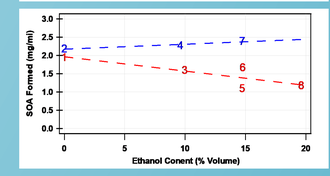
- Similar aerosol evolution during the photooxidation experiments in the chamber:
  - All fuels showed a broad, unimodal peak that did not shift during the experiment
  - The majority of the mass formation that occurred, was due to a small subset of particles that grew, and separated from the initial distribution.
  - The density of the smaller diameter mode of particles maintained a fractal morphology
  - The larger diameter mode particles were measured to have an average density of ~1.78 g cm^{-3} after separating from the initial peak, consisted with the density of AN



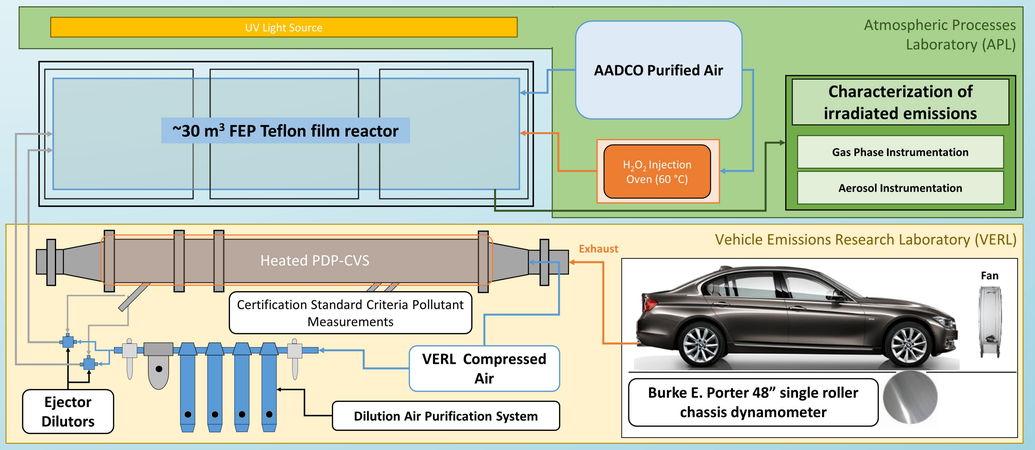
- High aromatics have largest SOA formation & largest total carbonaceous mass
  - Increasing aromatics led to higher SOA production
  - Higher SOA formation for the high PMI fuels with increasing ethanol content – A possible charge evaporative cooling effect will influence both the primary PM and SOA
  - A trend towards lower SOA formation for the low PMI fuels
  - The splash blends (F5 & F8) showed lower SOA formation – combination of oxygen content and aromatics dilution
  - Overall, lower SOA formation with higher ethanol fueling







Test Facilities: Vehicle Emissions Research Laboratory (VERL) & Atmospheric Processes Laboratory (APL):



Conclusions & Future Work:

- Tailpipe particulate emissions had strong relationship with the aromatic content
  - Positive Correlation with ethanol (within aromatic subgroups)
- High Aromatic Fuels formed the highest amount of secondary aerosol
  - Secondary Aerosol was dependent on the NH_3 emissions
- SOA formation was dependent on fuel composition
  - ↑ **Aromatic = ↑ SOA (SA)**
  - ↑ **Ethanol = ↓ SOA (SA)**
- Less volatile fuel properties (T70, T90, and C_{10+} Aromatics) also correlated with SOA formation
- Non-oxygenated fuels will produce more SOA than oxygenated fuels
- Possible ethanol evaporative cooling for the high PMI fuels affected the production of SOA
- Positive correlation with PMI
  - In future an SOA-focused PMI may improve PMI correlation to SOA formation

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