SVOC emissions from diesel trucks operating on biodiesel fuels


8/22/2017

Office of Research and Development (ORD)—National Risk Management Research Laboratory (NRMRL)
Motivation

- The 2007 Energy Independence & Security Act (EISA) mandated renewable fuel use in the transportation sector
- EPA sets Renewable Fuel Standards (RFS) annually (flexibility)
- 36 billion gallons of renewable fuels by 2022

Volumes Used to Determine the Proposed 2014 Percentage Standards

<table>
<thead>
<tr>
<th>Category</th>
<th>Volume$^a$</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulosic biofuel</td>
<td>17x10^6 gal</td>
<td>8-30x10^6 gallons</td>
</tr>
<tr>
<td><strong>Biomass-based diesel (FAMES)</strong></td>
<td>1.3x10^9 gal</td>
<td>1.3x10^9 gal$^b$</td>
</tr>
<tr>
<td>Advanced biofuel (non-corn EtOH)</td>
<td>2.2x10^9 gal</td>
<td>2.0-2.5x10^9 gal</td>
</tr>
<tr>
<td><strong>ΣRenewable fuel</strong></td>
<td>15.2x10^9 gal</td>
<td>15.0-15.5x10^9 gal</td>
</tr>
</tbody>
</table>

$^a$ All volumes are ethanol-equivalent, except for biomass-based diesel which is actual

$^b$ EPA is requesting comment on alternative approaches and higher volumes

As part of these requirements, EPA must:
- Assess the impacts of changes in ethanol volume and other fuel properties on emissions and ambient concentrations of air toxics and criteria pollutants
- Ensure “anti-backsliding” of air quality impacts and propose regulations to mitigate any adverse air quality impacts
Biodiesel study facts

• Roughly, $150 \times 10^9$ L of on-highway diesel produced annually in the U.S. of which $5 \times 10^9$ is biodiesel
• In many cases, biodiesel use actually reduces criteria pollutant emissions
• Water-soluble OC in PM can increase producing toxicological concerns
• To date, limited emphasis on the gas-phase SVOC emissions and the effect of increasing fuel oxidants
• MOVES model requires emissions information from this engine class
• As of 2016, greater than half of all vehicle miles travelled were for trucks with catalytic control for NOx and PM.
Diesel emissions control history

- **1998**: DOC
- **2004**: Optional DOC, Fuel Injection
- **2007**: DOC, Fuel Injection
- **2007**: CDPF, Fuel Injection
- **2010**: L/MHDDE, CDPF
- **2010**: M/HHDDE, CDPF, Urea Injection
- **2010**: AMOX, Urea Injection

**Emission Standards**
- PM ≤ 0.10
- NOx ≤ 4.0
- HC ≤ 1.3
- PM ≤ 0.01
- NOx ≤ 2.5
- NMHC ≤ 0.50
- PM ≤ 0.01
- NOx ≤ 1.4
- NMHC ≤ 0.14
- PM ≤ 0.01
- NOx ≤ 0.20
- NMHC ≤ 0.14
- PM ≤ 0.01
- NOx ≤ 0.20
- NMHC ≤ 0.14

**Regeneration Methods**
- Active regeneration
- Passive regeneration
Experimental – HD Vehicles (6.7L)


- 2011 Dodge Ram 2500
  - GVWR = 9,600 lb
  - DOC/NAC/CDPF
  - 35,498 km
  - HDV2B

- 2011 Ford F550
  - GVWR = 19,500 lb
  - DOC/SCR/CDPF
  - 4,333 km
  - HDV5

- 2011 Ford F750
  - GVWR = 25,999 lb
  - DOC/SCR/CDPF
  - 5850 km
  - HDV6

Active CDPF regeneration
Experimental – Testing

Clark et al. SAE Technical Paper, 2003-01-3284

- Test variables
  - Fuels: ULSD and B20 (soy)
  - Weight: laden/unladen (F550)
  - Temperature: -7 °C and 22 °C (F750)
  - Regeneration (WS-UDDS only)
  - Operating cycles (CS and WS-UDDS)
constant volume sampler
1:10 dilution

- 47 mm quartz fiber filter-PUFs
- OC-EC (mod. NIOSH Method 5040)
- SVOC, particle-phase and gas-phase speciation (TE- and SE-GC-MS)
- Artifact using ($Q_b$)

collected CS and UDDS-WS phases over $N \geq 3$
Experimental – Chemical Analysis

Thermal optical analysis (TOA; Sunset Labs)

Thermal optical transmission (TOT; NIOSH 5040 modification)
OC-EC Results

- OC is likely gas-phase due to $Q_b$
- Some background contribution
- EC slightly underestimated
- Limited if any pyrolysis

- More organic matter for this vehicle
- Less EC in general
- More OC associated with UDDS-WS
Experimental – Chemical Analysis ($Q_f$)

Thermal extraction system (TE; Gerstel Inc.)

- Sample introduction (> 6 μg of OC) (deactivated, pre-conditioned quartz tube)
- He flow (50 cc/min)
- Liquid N$_2$ coolant maintains tube at 25 °C before and after extraction step
- TE oven – programmable temperature control ramped at 50 °C/min from 25 to 325 °C
- GC-cooled, programmable temperature vaporization inlet system (CIS-PTV); quartz wool packed; ~80 °C during thermal extraction; heated to 300 °C at 720 °C/min) splitless transfer modes (TE, CIS-PTV)
- MS used in SIM mode

Short-path (152 mm) heated (325 °C) transfer line (SilcoSteel)

Experimental – Chemical Analysis (PuF)

- Manual solvent extraction
- DCM:hexanes:acetone [20:50:30]
- GC-MS (qqq) in MRM mode
- ~200 target analytes (n-, c-, and b-alkanes, PAH, oxy-PAH, Steranes/hopanes, aromatic acids, etc.)
- Focus on non-polar compounds
- All data are background subtracted
Data distribution frequencies

For OC-EC analysis:
- \( N = 64 \)
- Cycle and fuel data evenly distributed
- DPF data not represented

For SVOCs:
- \( N = 4574 \)
- Missing values = 3474
- B20 slightly more data (300 data points)
- PAH and alkanes drive analysis
Test-averaged, carbon-based pollutant emissions factors

- Outlier – red circle
- Mean – bold line
- Median – thin line
- 25th and 75th percentiles – box end
- 10th and 90th percentiles – whiskers
- ∑SVOCs – identified Q-Puf array

- Classic emissions trend
- Reduced/oxidized species show anti-correlation
- THC includes CH₄ and likely some OC and SVOC

Emission factors (g/km)

increasing volatility
OC-EC emissions trends – by Temp, fuel, and vehicle

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>V1</th>
<th>V2</th>
<th>V3</th>
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</table>

- **EC decreases with B20 on average**
- **lower chamber T --> higher mean EC emissions**
- **higher chamber T – wider EC range**
- **EC, CS > UDDS-WS**
- **mostly Dodge RAM 2500 data**

**OC**
- **OC increases slightly with ULSD**
- **CS >> UDDS-WS**
- **effect of chamber T is unclear**
Chemical Analysis – Results (T, VTW, fuel, and vehicle combined)

Cold start

PUF >> Quartz (mostly gas-phase)

CS > UDDS/WS
Chemical Analysis – SVOC class trends (combined by VTW and fuel)

- Gas-phase SVOC emissions dominate (90% w/w)
- CS >>> WS-UDDS
- Lower test T produce higher SVOC emissions
  - PAH/alkanes were most sensitive
- Active regeneration had no effect on SVOCs
- Switch to B20 had no effect on SVOCs
- VTW had no effect
- 538 µg/km mean sum
Multi-study heavy-PAH emissions comparison

- Tests conducted over several decades
- PAH emissions are highly variable
- Dynamometer emissions projections may be biased low
  - Cao et al. 2017
- Past studies indicated DPF sufficiently control PAH
- Our study shows PAH at the low-end of the uncontrolled emissions
- Passive CDPF regeneration systems show potentially significant PAH emissions
Conclusions for L/MHDDVs used presently

I. CO$_2$ dominates vehicle emissions and may have increased due to DOCs
II. Carbonaceous particle emissions are muted following CDPF after-treatment
III. For SVOCs: [gas-phase] >> [particle-phase]
IV. Driving cycle and T strongly affect SVOC emissions -- CS >> UDDS-WS
V. VTW, **fuel**, and regeneration had limited, if any, influence on SVOC emissions
VI. Passive CDP regeneration potentially increase PAH emissions
VII. Continue on-road testing to complement dynamometer studies