Measurement of diesel solid nanoparticle emissions using a catalytic stripper for comparison with Europe’s PMP protocol

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Background

• Gravimetric method reaches its limit to accurately measure diesel particle emissions.

• One cannot take advantage of DPF technology.

• Europeans recognized this problem and came up with a solid particle counting method a.k.a European PMP method, which counts particles larger than 23 nm (due to repeatability).
Background

• Issues with excluding sub 23nm particles in solid particle number counting.
  – Exclusion of ash particles.

• Issues with including sub 23nm particle in solid particle number counting.
  – Artifact particles can exist in this size range.
Objective

• Investigation of the nature of sub 23nm particles downstream the PMP system.
  – Existence and nature of sub 23nm particles

• Evaluation and comparison of the PMP system and catalytic stripper.
Particle measurement programme (PMP)

PMP system

Red: Semivolatile particles
Black: Solid (mostly soot) particles

 Courtesy of William Robertson at CARB
Why only particles larger than 23nm?

- $D_{50}=23$ ensures soot particles are measured but limits detection of any nucleation mode particles that escape the evaporation tube.

Giechaskiel et al. (2009) SAE 2009-01-1767

- $Sulfate > HC > Ammonium$  
Biswa et al. (2009)

Figures courtesy of D. Kittelson

Figures courtesy of H. Burtscher (2005)
Issues with not counting sub 23nm particles
Engine out, light-load, low soot conditions: Most of the number emissions are solid with $D_p < 23$ nm.

Cummins 2004 ISM engine, AVL modes

Courtesy of Dr. Kittelson
Spark ignition engines can also produce tiny solid nanoparticles, especially with metal additives.

Euro 3 passenger car, 10 ppm Mn in fuel, data courtesy Johnson-Matthey

Courtesy of Dr. Kittelson
Catalytic stripper (CS)

- **Sulfur-trap (S-Trap):**
  - Wall temperature: 300°C
  - Length: 11 cm
  - Diameter: 3.2 cm
  - $\text{BaO} + \text{SO}_3 \rightarrow \text{BaSO}_4$

- **Oxidation catalyst:**
  - Wall temperature: 300°C
  - Length: 11 cm
  - Diameter: 3.2 cm
  - 75 g/ft$^3$ of Pt

- Particle penetration
  - 5% at 3 nm
  - 75% at 100 nm

Test conditions

• Tests with exhaust aerosols from heavy-duty vehicle operating on chassis dynamometer.

  – Freightliner class 8 truck with 14.6 liter, 2000 Caterpillar C-15 engine, equipped with Johnson Matthey Continuously Regenerating Trap (CRT™)
  – Two steady state cruise conditions, constant speed 56 mph at 26% and 74% of full load

• Tests with laboratory-made challenge (or surrogate) aerosols without using an engine.
Measurement Diagram for Chassis Test

- **CVS**
  - cyclone particle cut point 2.5 µm
  - PMP system (=APC)
    - 1st dilution
    - 2nd dilution
    - DR=100 or 500

- **EEPS**
- **CPC 3022A_CVS**
- **CPC 3772_CS**

- **CPC 3772**
- **CPC 3776**
- **CPC 3025A**
- **nano-SMPS**

- **Ball valve**
- **Vent**
- **Venturi**
- **Ejector**
- **Compressed air**
- **Catalytic stripper**
- **Heated line**

- **Needle valve to vacuum**
- **Rotameter**

Alternate between the APC and CS
CVS particle size dist. measured by EEPS

74% engine load

26% engine load

EEPS data near noise level at 26% engine load
The PMP compliant system closely tracks the accumulation mode (74% load)

<table>
<thead>
<tr>
<th>CPC</th>
<th>$D_{50}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3790_APC</td>
<td>23</td>
</tr>
<tr>
<td>3772_CS</td>
<td>10</td>
</tr>
<tr>
<td>3025A</td>
<td>3</td>
</tr>
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<td>3772</td>
<td>10</td>
</tr>
<tr>
<td>3776</td>
<td>2.5</td>
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</tbody>
</table>
Comparison of particle concentrations at 74% load

- **Downstream of PMP system**
  - 3790 and 3772 agree – no particles between 10 and 23 nm
  - 3025A and 3776 agree and read progressively higher than 3772 and 3790 as time goes on – particles forming between 3 and 10 nm
  - Same trend at 100 and 500 dilution ratio

- **Downstream of CS**
  - In first time window all instruments agree – no particle below 23 nm
  - In second and third time windows 3776 and 3025A read higher than 3772 – particle formation between 3 and 10 nm

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</table>
Comparison of instruments at 26% load cruise

- Much lower concentrations than at 74%
  - Downstream of PMP system
    - In first time window, DR = 500
      - 3790 and 3772 agree – no particles between 10 and 23 nm
      - 3776 and 3025A read much higher and disagree – many particles below lower cutoff size of these instruments, 2.5 to 3 nm
    - In second time window, DR = 100
      - 3790 and 3772 read higher but agree – no particles between 10 and 23 nm but formation above 23 nm
      - 3776 and 3025A agree but read only slightly higher than 3790 and 3772 – nearly all particles have grown to above 23 nm
  - Downstream of CS
    - Consistently lower reading and agreement between instruments

- In last time window instruments bypass volatile particle removal systems and are directly connect to CVS – measure total solid and volatile particles – fewer particles than DR = 500 APC, clear evidence of particle formation by APC
Lab test (similar to Swanson and Kittelson)

1st dilution at PMP (150°C)
2nd dilution at PMP

Evaporation tube (300°C)
Catalytic stripper

Mixture heat to 250°C

Penetration efficiency by total particle number

<table>
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<tr>
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<th>PMP (=APC)</th>
<th>CS</th>
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<tr>
<td>H₂SO₄ + HC</td>
<td>0.6%</td>
<td>0.55%</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.1%</td>
<td>0%</td>
</tr>
<tr>
<td>HC (C₂₄ or C₄₀)</td>
<td>1%</td>
<td>0%</td>
</tr>
</tbody>
</table>

![Penetration efficiency graph](graph.png)
APC ET temperature oscillation

Lab test

Hydrocarbon heat and evaporate

Sulfuric acid heat and evaporate

Mixture heat to 250°C

Chassis test (74% load)

Cyclone

PMP (=APC)

CPC 3790

CVS

Cyclone

PMP (=APC)

CPC 3790

CPC3776

a

Laboratory test: sulfuric acid and tetracontane

PMP (=APC)

CPC 3790 (23nm)

ET temperature

Number Concentration (#/cc)

Time (s)

b

ET temperature

CPC 3776 (3nm)

CPC 3790 (23nm)

Accumulation mode particles

Number Concentration (#/cc)

ET Temperature (°C)

Time (s)
Conclusion

• Volatile remover such as the PMP system and the CS makes substantial number of sub 10nm particles.
• The sub 10 nm particles downstream the PMP were formed in the PMP system, because:
  – Particle concentration of those sub 10 nm particles oscillated in relation with the oscillation of the PMP ET temperature.
  – Some of these appeared to be solid as they could not be removed by the CS in the lab experiment others appear to be semivolatile as they fluctuated along with ET temperature.
Implication and future work

- The PMP works fine with $D_{50}=23\text{nm}$, but if PMP needs to measure ash particles and be applied more widely with a lower or no cutoff diameter then the PMP needs to be improved not to make artifact particles.

- New $D_{50}$ for PMP=10nm?

- Do sub 10nm particles exist in other vehicles and cycles?
  - e.g. HD 2010 compliant OEM, GDI, & transient cycles
  - More experiments are needed.

- More controlled study (e.g. lab study) is needed to better understand the particle formation process.
Acknowledgements

• **CARB**
  – For funding and instruments.
  – A. Ayala and J. Herner for encouraging this study.

• **AVL LIST GmbH Inc.**
  – Providing an AVL particle counter and technical support.
  – B. Giechaskiel, M. Linke, R. Frazee, S. Roeck, & W. Silvis

• **UCR/CE-CERT**
  – D. Pacocha, J. Valdez, and E. O’ Neil
  – P. Ziemann and D. Cocker

• **University of Minnesota**
  – J. Swanson

• **Johnson Matthey**
  – M. Twigg (For catalysts to assemble the catalytic stripper)
Five papers raise issues about solid particle measurements, especially when applied to particles smaller than 23 nm

- **Work done at University of California, Riverside, CE-CERT**

- **Work done at the University of Minnesota, CDR**

- **Work done at California Air Resources Board**
  - Herner et al. (2007). Investigation of ultrafine particle number measurements from a clean diesel truck using the European PMP protocol, SAE 2007-01-1114
Thank You