Similarities between soot properties from low temperature combustion in a heavy duty diesel engine and miniCAST flame soot

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Background

• In-situ optical diagnosis in flames: Immature (young) soot with high Absorption Angstrom Exponent (AAE) early in the flame (e.g. Michelsen et al. 2017)

• Soot generators based on quenched flames can result in ”soot rich in organic carbon” (e.g. Maricq et al. 2014, AS&T)

• High AAE in biomass combustion emissions is caused by: ”extremely low volatility organic aerosol” (Saleh et al. 2014, Science)

• Ship emissions from heavy fuel oil consist of insoluble tar components with high AAE (Corbin et al. 2018 JGR)
Aims:

• Investigate optical, chemical and structural properties of emissions from:
  • Paricle emissions from a quenched diffusion flames (mini-CAST)
    • Varied N₂ dilution of fuel flow and air to fuel ratio
  • Low temperature combustion in HD diesel engine
    • From no to very high EGR
  • Particles extracted from inside the cylinder during the diesel combustion process
    • Variations from soot formation to soot oxidation phase
Methods – Mini CAST emissions

- Thermal optical analysis (OC/EC) using EUSAAR_2 protocol
- AAE and eBC from Aethalometer and in-situ Extinction cell
- Aerodyne SP-AMS (1064 nm IR Vaporisation)
  - Laser off: Quantification of particulate PAHs (202 - 302 Th, Malmborg et al. 2017)
  - Laser on: Carbon cluster distribution from soot cores

<table>
<thead>
<tr>
<th>OP</th>
<th>Propane (L min⁻¹)</th>
<th>Air-oxid (L min⁻¹)</th>
<th>N₂-mix (L min⁻¹)</th>
<th>N₂-quench (L min⁻¹)</th>
<th>Air-dil (L min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.55</td>
<td>0</td>
<td>7</td>
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<td>1.36</td>
<td>0.300</td>
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<td>0</td>
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</tbody>
</table>

Török et al. 2018 AS&T
Wavelength dependent absorption

Török et al. 2018 AS&T
BC fractions depends on what reference mass is chosen

- Also has implications when calculating Mass Absorption Cross Sections
Changes in Particle Composition

Increasing adiabatic flame temperature

- 100 ml/min $N_2$
  *Longer, turbostratic, nanostructures*

- 300 ml/min $N_2$
  *Short, amorphous, curved nanostructures*

MiniCAST soot generator

OP3

HRTEM

25°C

"Mature" soot

9% EC
91% OCEC

OP7

"Immature" soot

Low volatility "organic" carbon

53% OC
34% PC
26% 50%
Changes in Particle Composition

Increasing adiabatic flame temperature

100 ml/min \( \text{N}_2 \)
Longer, turbostratic, nanostructures

300 ml/min \( \text{N}_2 \)
Short, amorphous, curved nanostructures

“Mature” soot

“Immature” soot

“Elemental” carbon

Low volatility “organic” carbon

HRTEM

OCEC

25°C

500°C

“Elemental” carbon

Low volatility “organic” carbon

SP-AMS

OP3

OP7

MinicAST soot generator

Malmborg et al. 2018 Submitted
Low Temperature Combustion in HD Diesel Engine - Methods

- Scania Heavy-Duty D13 engine modified to 1 cylinder operation.
- Bore 130 mm, stroke 160 mm, compression ratio 17.3, cylinder volume 2.1 l.
- Exhaust gas recirculation (EGR) sweep from 21 to 8% inlet $O_2$.
- Fuels: MK1 Diesel, HVO, RME
- No after treatment
- Low load: 6 Bar IMEP (~20%)
Influence of EGR on Emission Levels

Graph showing the effect of intake O₂ on emissions of HC, NOx, and CO. The graph indicates that as intake O₂ increases, HC and NOx emissions decrease, while CO emissions increase. The legend shows different fuel blends (B0, B20, B100) and the figure highlights the differences in total particle mass for High EGR and No EGR conditions.
Absorption Angstrom Exponent vs EGR level (HVO)
Effect of EGR on Particle Composition (HVO)
In-cylinder diesel soot characteristics investigated with on-line aerosol mass spectrometry

Single cylinder heavy duty diesel engine

Evolution of particle properties over the combustion cycle – HD diesel engine
Similarities between miniCAST and HD diesel engine exhaust
Conclusions

• Similarities in composition and optical properties of PM from:
  • miniCAST with high N₂ fuel dilution
  • Low temperature combustion in HD diesel engine
  • Soot formation phase in HD diesel engine

• High AAE (Brown Carbon)

• Persistent “organic” carbon that pyrolyse upon heating in inert gas
  • Linked to large carbon fragments in SP-AMS mass spectra

• Structural properties changes (reduced fringe length in TEM)

• This may be the intersection of organic carbon and immature soot!
  • We may detect Black Carbon Precursors (BPC) that has not matured to BC

• Future work
  • What are the health effects of this new class of carbon?
Acknowledgements

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