Measurement and Characterisation of Aerosols from Engine Combustion Processes

Dr Jon Symonds
Technical Manager
Cambustion, U.K.
Contents

- Overview of engine particulate emissions
  - Characteristics
  - Formation
  - Evolution
- Legislation – the drive for measurement
- What do we wish to measure & how can we measure it?
  - Overview of engine emissions testing
  - Mass
  - Opacity
  - Number
  - Size
  - Density
- Control technologies
- Future Developments
Types of IC Engines

• Compression Ignition (Diesel)
  - Spontaneous ignition, due to compression temperature
  - Diffusion flame
  - Mixture locally rich in fuel plume as mixing occurs

• Spark Ignition (Gasoline / LPG / CNG)
  - Port fuel injected:
    *Stoichiometric* air:fuel ratio required for 3-way catalyst operation, low P.M. emission (pre-mixed flame)
  - Gasoline Direct Injection (GDI), higher compression, greater efficiency…
  - … but fuel / air less well locally mixed → more P.M. (semi-diffusion, semi-pre-mixed)

• Two-stroke
  - Air, fuel and oil mixed
  - P.M. high due to burnt (and aerosolised) oil
Particle emissions from Diesel engines

- Number or mass weighted size spectrum contains 3 modes:

- **Engine:**
  - Carbonaceous
  - Organic
  - Sulphate
  - Ash

- **Other (Coarse):**
  - Brake dust
  - Tyre wear
  - Road wear
  - Rust & scale

D.B. Kittelson, Centre for Diesel Research, University of Minnesota, U.S.A.
Particle formation in engines – soot

- Air:fuel ratio (AFR) critical – “rich” or “lean”
- Stoichiometric HC combustion produces \( \text{H}_2\text{O} \) & \( \text{CO}_2 \)
- As oxygen levels drop: \( \text{CO}_2 \rightarrow \text{CO} \rightarrow \text{C} \)
- Short timescales: localised AFR can be very different to overall AFR
Particle formation in engines – ash, volatile fractions

- Ash formed from inorganic molecules in fuel, oil, additives + engine wear e.g. metal oxides. Tend not to aggregate, < 50 nm

- Sulphuric acid formed from sulphur in lube oil and fuel, which forms SO$_2$ during combustion, followed by

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \xrightarrow{H_2O} H_2SO_4$$

Catalysed by Diesel Oxidation Catalyst…

- Organic fraction:
  - Un-burnt or partially burnt fuel (fuel pools, PAH)
  - Lubrication oil (both from cylinder and crankcase, inc. coarse mode droplets)

- Volatile fractions do no enter the “particulate phase” until cooling and dilution
Particle evolution – exhaust and beyond

- Cooling: Increase in saturation ratio, drives nucleation and growth
- Dilution: Decrease in partial pressures, suppresses nucleation and growth
- Initial cooling caused nucleation, “real world” dilution eventually freezes (or reverses) process

![Graph showing particle size distribution](image-url)
### Legislation

#### Europe:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Date</th>
<th>Diesel PM (mg/km)</th>
<th>Diesel PN (#/km)</th>
<th>Direct Injection Gasoline PM (mg/km)</th>
<th>Direct Injection Gasoline PN (#/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro 3</td>
<td>Jan 2000</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 4</td>
<td>Jan 2005</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5a</td>
<td>Sept 2009</td>
<td>5*</td>
<td>-</td>
<td>5*</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5b</td>
<td>Sept 2011</td>
<td>5*</td>
<td>6.0 × 10^{11}</td>
<td>5*</td>
<td>-</td>
</tr>
<tr>
<td>Euro 6</td>
<td>Sept 2014</td>
<td>5*</td>
<td>6.0 × 10^{11}</td>
<td>5*</td>
<td>6.0 × 10^{12} (6.0 × 10^{11} from 2017)</td>
</tr>
</tbody>
</table>

European light duty particulate emission standards – Source dieselnet.com. *4.5 mg/km if measured by the PMP procedure

#### US:

- Mass based standards for light duty, heavy duty, non-road marine and rail
- California does its own thing – mass based but now considering number
Euro V / VI: The Particle Measurement Programme

- United Nations Economic Commission for Europe (UNECE) commissioned – Introduced a **Solid Particle Number** metric

- Addresses limitations in and criticism of filter paper method
  - Lack of sensitivity & repeatability for ever cleaner engines – mass mostly condensed gas phase volatiles
  - Biased to larger particles, yet smallest particles have greatest health effects

Data courtesy of Chris Parkin, UK DfT
The Emissions Lab – Dynamometer Testing

- Dynamometer supplies load to engine
- Vehicle driven on standard driving “cycle”

**New European Drive Cycle (NEDC)**

**Federal Test Procedure (FTP) 75**
The Emissions Lab – Sampling and Dilution

- Constant Volume Sampler (CVS) Tunnel:
  - Variable dilution of exhaust (variable exhaust flow, constant CVS flow)
  - All particles (or gas molecules) end up in CVS flow; CVS flow is known and constant:

\[
\text{mass (or number) rate} = \text{mass (or number) concentration} \times \text{CVS flow}
\]

\[
\text{mg/s} = \text{mg/cc} \times \text{cc/s}
\]

\[
\text{total mass} = \int \text{mass rate} \, dt
\]

\[
\text{specific mass (mg / km)} = \frac{\text{total mass}}{\text{distance}}
\]
Mass Measurement (1)

- Gravimetric (Filter Paper)

  • Filter Paper Reflectance (Smoke Number)

  e.g. AVL 415

Weigh before and after
Mass Measurement (2)

- Photo Acoustic Soot Sensor / Micro Soot Sensor

  - Tuned resonant cavity
  - Light source
  - Microphone

  e.g. AVL 483 MSS

- Tapered Element Oscillating Microbalance (TEOM)

  - Filter
  - Excitation / Detection Transducers
  - Quartz Tube

  e.g. Air Monitors TEOM-FDMS
Opacity

- Used for MOT testing
- Still used for some approval regulations

\[
L = L_{\text{eff}}
\]

e.g. AVL Opacimeter
VPR evaporates liquid particles to less than 23nm

CPC has declining counting efficiency below 40nm (e.g. only 50% of 23nm particles are counted)

Output from CPC corresponds closely to solid particle number concentration

e.g. Horiba SPCS, AVL Particle Counter (APC) 489

\[ DF_{TOTAL} \propto \frac{T_1(MFC_1 + MFC_2)}{f_{DISC}} \]
Condensation Particle Counter (CPC)

Flow Metering & Pump

Laser

Detector

Condenser ~ 14°C

Butanol

Inlet

Saturator wick ~ 39°C
Size Measurement

• Aerodynamic Diameter

Electrical Low Pressure Impactor (ELPI – Dekati):

• Electrical Mobility (drag:charge) Diameter:
  • Scanning Mobility Particle Sizer (SMPS, e.g. TSI or Grimm)

• Differential Mobility Spectrometer (fast)….
Differential Mobility Spectrometry (1)

- Particles charged by corona charger
- Particles carried by sheath flow, deflected by high voltage electrode
- Particles land on 1 of 22 detection rings, which measure small currents
- Inversion algorithm converts electrical mobility to size spectrum
- Mass and number calculated from size spectrum
Differential Mobility Spectrometry (2)

Commercial versions: Cambustion DMS500 & DMS50; TSI EEPS & FMPS
The Need for Fast Response

- DMS responds to fast changes in AFR control due to fast time response
Centrifugal Particle Mass Analysers

Diagram courtesy of J. Olfert

\[
\frac{m}{N_q} = \frac{eV}{r^2 \omega^2 \ln \left\{ \frac{r_o}{r_i} \right\}}
\]

Commercial versions: Cambustion CPMA & Kanomax APM 3600 and 3601
CPMA Density Measurements

Aerosol → DMA → CPMA → CPC

50 nm Diesel soot

Effective density

Mass:mobility relationship

Symonds et al., 2011
Control Technologies

• Control by engine development / calibration
  - EGR
  - Injection strategy
  - Boost control

• Control by filtration: Diesel Particulate Filter (DPF)
  - Good solution for removing *solid* particles (effectively mandated by Euro VI for Diesel)
  - Require periodic regeneration

S. Payne, 2011
DPF filtration efficiency

DPF Filtration Efficiency - DPG

Number based filtration efficiency %

Cake filtration mode

Pore bridging mode

soot load g
Gasoline Direct Injection

Peckham, Campbell & Finch, 2011
Future Developments (1)

- World harmonised test cycle (WLTP – World harmonised Light vehicles Test Procedure)
- In use compliance, via Portable Emissions Measurement Systems (PEMS)

Europe
- Adoption of WLTP
- Real Driving Emissions (RDE)
- Non-road Mobile Machinery (NRMM)

USA
- LEV3 (Low Emissions Vehicle) – California
- Tier 3 emissions (Light duty)
- Tier 4 – Non-road
Future Developments (2) – In use compliance

- Real world driving highly transient, and “unrepeatable”

DMS50 data
Symonds et al. 2007
Conclusions

• Europe moving from mass to number, US may follow

• Fast time response vital for development work using transient cycles

• DPFs effectively solve solid P.M. emissions from Diesel

• Debate continues as to the wisdom of ignoring the small particles in the PMP metric

• PM reduction research now concentrating on GDI

• Real-world driving emissions increasingly important
Cambridge, U.K.

Jon Symonds: jps@cambustion.com

www.cambustion.com