Nanoparticle Emissions from Internal Combustion Engines

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Ultra Fine Particles in the Atmosphere
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Engine Exhaust Particle Emissions:
Some Current Issues
Outline

• Background
• Formation and character of exhaust particles
• Nuclei mode formation and growth
• Role of carbonaceous agglomerates
• Summary and Conclusions

Most of the recent U of M experimental work reported here was performed by Dr. Imad Abdul-Khalek and Mr. Qiang Wei with funding from Perkins Engine Company.
Emissions of Ultrafine and Nanoparticles from Engines

• Current emission standards are mass based. Recently interest in other measures, i.e, size, number, surface, has increased.

• Concerns about particle size
  – New ambient standards on fine particles
  – Special concerns about ultrafine and nanoparticles
  – Indications that reductions in mass emissions may increase number emissions

• Difficulties associated with measurement of ultrafine and nanoparticles
  – Often more than 90% of particle number are formed during exhaust dilution
  – Particle dynamics during sampling and dilution are highly nonlinear - large changes in of particle number may result from small changes dilution and sampling conditions
Typical Diesel Particle Size Distribution - Log Scale

Typical Engine Exhaust Size Distribution
Both Mass and Number Weightings are Shown

Normalized Concentration, $dC/C_{total}/d\log Dp$

- **Fine Particles** $Dp < 2.5 \mu m$
- **Ultrafine Particles** $Dp < 2.5 \mu m$
- **Nanoparticles** $Dp < 50 \text{nm}$
- **Nuclei Mode**
- **Accumulation Mode**
- **Coarse Mode**

- **PM10** $Dp < 10 \mu m$
The new engine increased number emissions 10 to 30 fold!

HANCOCK, 1979 roadway measurements made on behind a truck powered by an engine of the same family showed high nanoparticle emissions! Other roadside and on road measurements made since the late 60's have shown high nanoparticle emissions.

The new engine sharply reduced mass emissions, by about a factor of 3.
Nanoparticles in the atmosphere appear to be associated with both spark ignition and diesel engines.
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Typical Composition of Diesel Particulate Matter: Lube oil contributes to SOF, ash, sulfate

![Pie chart showing the composition of diesel particulate matter:]
- Carbon: 60%
- Ash: 13%
- Sulfate and Water: 7%
- Lube Oil SOF: 10%
- Fuel SOF: 10%
Particles consist mainly of highly agglomerated solid carbonaceous material and ash and volatile organic and sulfur compounds.
Particle Formation History:
From the Start of Combustion to the Nose

This is where most of the nanoparticles emitted by engines usually form.

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Studies of Diesel Nanoparticle Formation Using a Variable Residence Time Dilution System
Influence of Residence Time on Number Weighted Size Distributions

$T_{\text{dilution}} = 32 \, ^\circ\text{C}$,
Primary DR $\sim 12$

1600 rpm, 50% load
Influence of Dilution Temperature on Number Weighted Size Distributions

Residence Time ~ 400 ms, Primary DR ~ 12
Humidity Ratio ~ 0.0016

1600 rpm, 50% load
Influence of Primary Dilution Ratio on Number Weighted Size Distributions

- Primary Dilution Ratio (PDR) ~12
- Primary Dilution Temperature (PDT) ~ 48 °C, Residence time ~1000 ms, HR ≤ 0.0016
- PDR ~ 25
- PDR ~ 40
- 1600 rpm, 50% load
Our results suggest nanoparticles are mainly volatile, we have demonstrated this with a catalytic stripper.
Typically more than 99% of the nanoparticles disappear by 300 °C (except with metal additives)
Which Volatile Materials in the Exhaust Are Likely Precursors to Nuclei Mode Formation and Growth?

For typical diesel exhaust conditions, saturation ratio of hydrocarbons comprising the SOF may not be high enough for nucleation, $S > \sim 3$

**Influence of Dilution Upon Extractables**

Assumes extractable mass of 8 mg/m³ is nonodecane
Tex = 240 C, Ta = 27 C

These levels are too low for nucleation but would drive absorption and adsorption.
What does nucleate? Consider the threshold for Binary $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ nucleation

- An extreme dependence of the nucleation rate upon temperature, $\text{H}_2\text{SO}_4$, and $\text{H}_2\text{O}$ concentrations makes theoretical predictions of nucleation difficult.
- Seinfeld and Pandis give an empirical expression to predict the onset of nucleation in this system:

$$C_{\text{crit}} = 0.16\exp(0.1T - 3.5RH - 27.7)$$

where $C_{\text{crit}}$ is the threshold $\text{H}_2\text{SO}_4$ concentration in $\mu\text{g}/\text{m}^3$, $T$ is temperature, RH is relative humidity (0 to 1).
- I have used this expression and mass and energy balances applied to the dilution process to predict the ratio of the actual $\text{H}_2\text{SO}_4$ concentration to the critical one, $C/C_{\text{crit}}$. When this critical concentration ratio exceeds one, nucleation is likely.
Influence of Fuel and Exhaust Conditions on Sulfuric Acid Nucleation

Fuel sulfur conversion to sulfate = 3%,
Air-fuel ratio = 30, $T_{\text{air}} = 27$ C, RH = 40%
Influence of Fuel and Lube Oil Sulfur (courtesy C. Barnes, Perkins Engine Company)

11 Nov 1999, 3 ppm Sulphur, Normal Lube Oil
16/18 Nov 1999, 3 ppm Sulfur, Fuel + Low Sulphur Lube Oil
07 Jan 2000, 450 ppm Sulphur, Normal Lube Oil

Medium-Duty Engine, 1600 rpm, 10% Load
Sulfuric Acid Appears To Trigger Nucleation But Typical Concentrations Are Too Low To Produce Observed Particle Growth Rates

Maximum rates of particle growth and vapor depletion in free molecular regime. 400 PPM sulfur fuel, 3% sulfur to sulfate conversion, 15% RH, 0.4 m²/m³ soot surface area, 8 mg/m³ C_{19}H_{40} as hydrocarbon, Dilution ratio 12, T dilution 32 C

Growth rates of about 20 nm/s are observed for these fuel and dilution conditions
Nanoparticle Nucleation and Growth

- It appears that with current engines binary sulfuric acid - water nucleation triggers the process.
- The initial size of these nuclei is about 1 nm.
- In most cases there is not enough sulfuric acid present in the exhaust to explain the observed rates of particle growth.
- Hydrocarbons normally associated with the soluble organic fraction apparently are absorbed by the concentrated sulfuric acid nuclei leading to the observed growth rates.
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Carbonaceous Agglomerates Adsorb Volatile Particle Precursors and Suppress Nanoparticle Nucleation and Growth

- A time constant for molecular adsorption may be determined from the molecular collision frequency and the particle surface area available for adsorption.

\[ \tau_a = 1 / \left( \left( \frac{RT}{2\pi M} \right)^{0.5} A_p \right) \]

- Under typical roadway conditions the dilution ratio, $D$, of an exhaust plume varies roughly linearly in time so that a time constant for dilution can be defined as follows.

\[ D = 1 + t / \tau_d \]

- Then a dimensionless adsorption rate can be defined.

\[ R_{ads} = \tau_d / \tau_a \]
H$_2$SO$_4$ Nucleation and Growth Is Suppressed by Adsorption onto Carbon Agglomerates

Nucleation suppressed by increasing carbon concentration or slower dilution. Low exhaust carbon emissions and/or fast (roadway) dilution. More potential to form nanoparticles.

Increasing dimensionless adsorption rate

High exhaust carbon emission and/or slow (laboratory, congested traffic) dilution. Less potential to form nanoparticles.

H$_2$SO$_4$ / H$_2$O nucleation
500 PPM S fuel, 3% conversion
Texh = 330 C, Tair = 27 C, RH = 40%

Concentration Ratio C/Ccrit

Dilution Ratio

Rads = 0, 0.01, 0.02, 0.08, 0.27, 0.92, 3.20
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• A significant amount of particulate matter (e.g. 90% of the number and 30% of the mass) is formed during exhaust dilution from particle precursors that are in the vapor phase in the tailpipe (e.g., sulfuric acid, fuel and oil residues).
  – New particles are formed by nucleation. This is likely to be the source of most of the ultrafine and nanoparticles (and particle number) associated with engine exhaust.
  – Preexisting particles grow by adsorption or condensation.
  – Nucleation and adsorption are competing processes. Carbon agglomerates provide a large surface area for adsorption that suppresses nucleation.
  – Thus, engines with low carbon mass emissions may have high number emissions of volatile, but NOT solid particles.
  – It should be possible to reduce nanoparticle emissions by reducing emissions of sulfuric acid and hydrocarbons.
Nanoparticle measurements are very strongly influenced by the sampling and dilution techniques employed.

- Nucleation, adsorption, absorption, and coagulation during sampling and dilution depend upon many variables, including dilution rate, (or residence time at intermediate dilution ratio), humidity, temperature, and relative concentrations of carbon and volatile matter.
- Changes of more than two orders of magnitude in nanoparticle concentration may occur as dilution conditions are varied over the range that might be expected for normal ambient dilution, e.g., 0.1 to 2 s dilution time scales. Even larger changes may occur with engines that emit very little carbon.
- Carbon in the exhaust suppresses nanoparticle formation less effectively when the exhaust is diluted rapidly over a roadway than when it is diluted slowly.

Sampling systems should mimic atmospheric dilution to obtain samples representative of the tailpipe to nose process.
The most difficult problem associated with exhaust particle measurement is understanding the dilution process from tailpipe to nose -- this is being examined in the CRC E-43 program.
This illustration shows a typical application of the University of Minnesota Mobile Aerosol laboratory developed for the CRC E-43 Program.
Nanoparticles are produced by new engines, but concentrations may be much lower than feared.
Summary Diesel - 3

• Currently most of the particles in the nanoparticle size range are volatile. However, as engines become cleaner, metallic ash particles from the lubricating oil (or fuel if metallic additives are present) may become more important.
  – Solid particles raise new issues…
  – But they are easy to control with exhaust filters

• Spark ignition engines typically emit smaller particles than diesel engines and are an important source of fine particles and nanoparticles.
  – A recent study in Colorado concluded that up to 2/3 of the fine particle mass emitted by vehicles was from spark ignition engines
  – New gasoline direct injection engines emit much higher particle concentrations than conventional engines and may approach diesel levels under some conditions