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Nanoparticle Growth During Dilution and Cooling of Diesel Exhaust:

Experimental Investigation and Theoretical Assessment

Nanoparticle Growth During Dilution and Cooling of Diesel Exhaust: Experimental Investigation and Theoretical Assessment

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Outline

- Highlight of Current Important Issues
- Diesel Engine and Particle Nucleation
- Particle Measurement System
- Example of the Influence of Dilution Conditions on Particle formation and Growth
- Calculation of Growth rate from Experimental Data
- Prediction of Particle Driving Pressure and Stability
- Extrapolation of Size Distribution to 1 nm size
- Conclusions
- Acknowledgments
- Future Direction and Current Activities at SwRI

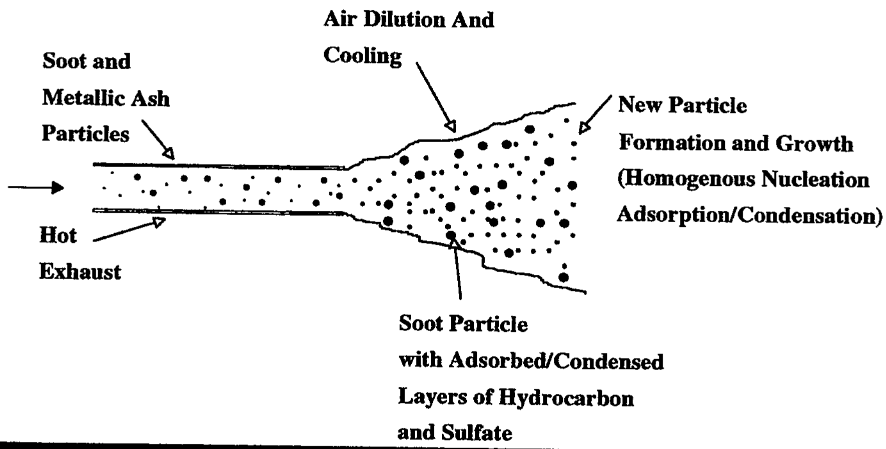
Highlight of Current Important Issues

- **Health**
  - **Nanoparticles, Ultrafine, Fine**
  - **Solid Vs Volatile particles**
- **Engine Technology**
  - **High Injection Pressure**
  - **Low Mass Emissions**
- **Aftertreatment Devices**
  - **Traps and Nanoparticle formation**
  - **Oxidation Catalyst and Nanoparticle formation**
- **Fuel and Lube Oil**
  - **Ultra Low Sulfur Vs Low Sulfur Vs High Sulfur**
  - **Lube Oil Contribution to Nanoparticles**
- **Measurements**
  - **Dilution Ratio, Dilution Temperature, Residence Time, Relative Humidity, Dilution System, Volatile and Solid Particles, Instrumentation Bias etc...**

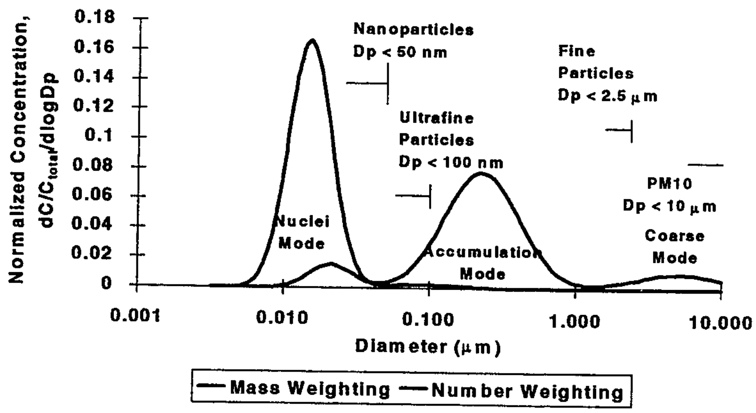
Diesel Engine and Particle Nucleation

- **Three Phases of Particle Nucleation May Be Caused by Diesel Combustion**
  - **First Phase: Soot During Combustion**
  - **Second Phase: Metallic Ash from Lube Oil During Expansion**
  - **Third Phase: Sulfuric Acid and Hydrocarbon during dilution and Cooling of Hot Exhaust**

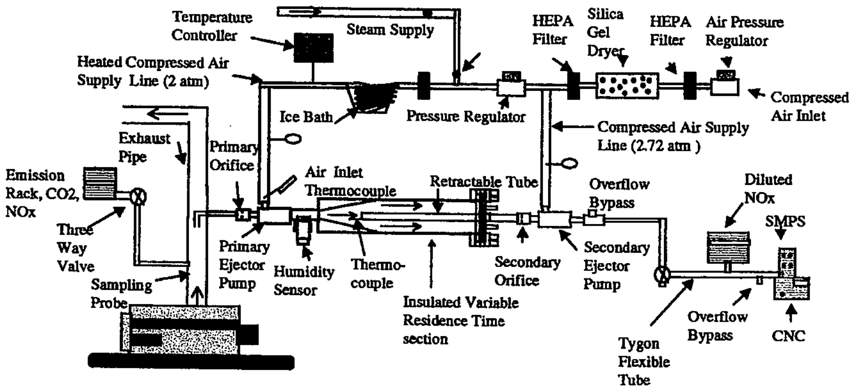
Particle Formation During Dilution and Cooling of Hot Exhaust



Ideal Diesel Engine Exhaust Particle Size Distributions



Particle Measurement with a Variable Residence Time Micro-Dilution System



Results (Engine Out Emissions)

- Example of the Influence of Dilution Conditions on Size Distributions
- Particle Growth Rate Determination
- Extrapolation of Size Distributions

Summary of Average Growth Rate at Different Dilution Conditions

Table 4.2- Average Diameter Growth Rates (nm/sec) at Different Dilution Conditions

	PDR=12 (HR = 0.004) D-2 Diesel	PDR=25 (HR = 0.003) D-2 Diesel	PDR=40 (HR = 0.0018) D-2 Diesel
PDT = 13°C	-	-	6.1 ± 1.5
PDT = 17 °C	-	8.6 ± 1.6	-
PDT = 32 °C	11.0± 0.5	10.7 ± 1.4	7.4 ± 0.8
PDT = 48 °C	16.0 ± 2.2	11.5 ± 2.3	1.8 ± 0.2
PDT 48 °C	13.7 ±1.1*		
PDT = 48 °C	24.1 ±7.0**		
PDT = 65 °C	17.5 ± 1.9	-	-

* This run is performed at 0.03 humidity ratio
** This run is performed with ultra low sulfur fuel
The Growth Rate Unit is in nanometer per second

Determination of Average Driving Pressure During volatile particle Growth

$$\Delta p = (P(t) - Pv) = \frac{\sqrt{2\pi m_m kT}}{2 v_l}\frac{dD_p}{dt}$$

P: Partial Pressure of vapor, Pv: Vapor pressure , m_m: molecular mass, vl: molecular volume, dDp/dt: Particle Growth Rate, k: Boltzmann's constant, and T is absolute temperature

Prediction of Exhaust Concentrations of Species from Particle Growth Data

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PDT	PDR	C16 (mg/m³)	C25 (mg/m³)	Pure H_2SO_4 (mg/m³)	80 % H_2SO_4 by mass (mg/m³)
32	12	9585	1.57	2.12	0.28
48	12	22837	6.03	9.78	0.49
48	12	22836	5.94	9.72	0.42
48	12	22838	6.35	9.94	0.67
65	12	56710	29.78	43.05	1.00
17	25	10003	1.15	1.13	0.45
32	25	19969	3.25	4.42	0.58
48	25	47575	12.21	20.16	0.77
13	40	14233	1.25	1.18	0.51
32	40	31947	4.75	6.83	0.66
48	40	76113	18.26	31.60	0.48

A sulfuric acid solution seems the best candidate for a growing droplet

Conclusions

- **Exhaust Particle Number Concentrations and Size Distributions were measured using a Variable Residence Time Micro-Dilution Tunnel and a Scanning Mobility Particle Sizer (SMPS)**
- **Average particle growth rate was calculated from size distributions at the same the dilution conditions and different residence times. A growth rate in the range of 10-20 nm/sec was observed at the primary dilution ratio.**
- **The driving pressure and thus the likely composition of a growing volatile particle was predicted from the growth rate data. Volatile particles match a sulfuric acid solution property. At a normal temperature of 20 °C, the evaporation rate in the atmosphere is on the order of 0.08 nm / sec. e.g a 23 nm droplet should vanish in 5 minutes. More work is needed to verify such possibility.**

Conclusions (Continued)

- A well controlled step dilution system is a valuable tool for understanding the influence of the dilution process on particle formation. More comprehensive fundamental study is needed to establish the proper criteria of diluting engine exhaust.

Acknowledgments

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Future Direction

- Particle size distribution measurements from engines should follow two routes:
  - The first route is to focus on the emissions and size of solid particles
  - The second route is to focus on the emissions and size of volatile droplets

Current Activities at SwRI

- Southwest Research Institute, together with the University of Minnesota, Particle Technology Laboratory, and Lovelace Respiratory Research Institute, are working on the development of a sampling train for particle size distribution measurement from engines, during transient testing, using ELPI and a newly developed Parallel Flow Diffusion Battery. Testing of the new sampling train will be evaluated at SwRI by the end of August. This work is funded by the Environmental Protection Agency

- SwRI recently proposed PM initiatives related to fine and ultrafine particle sizing activities. This includes the evaluation of various engine technologies, aftertreatment devices, fuels etc...