D. Kittelson
University of Minnesota
Minneapolis
USA

15

Influence of Sampling and Dilution Conditions on Nanoparticle Measurements

Influence of Sampling and Dilution Conditions on Nanoparticle Measurements

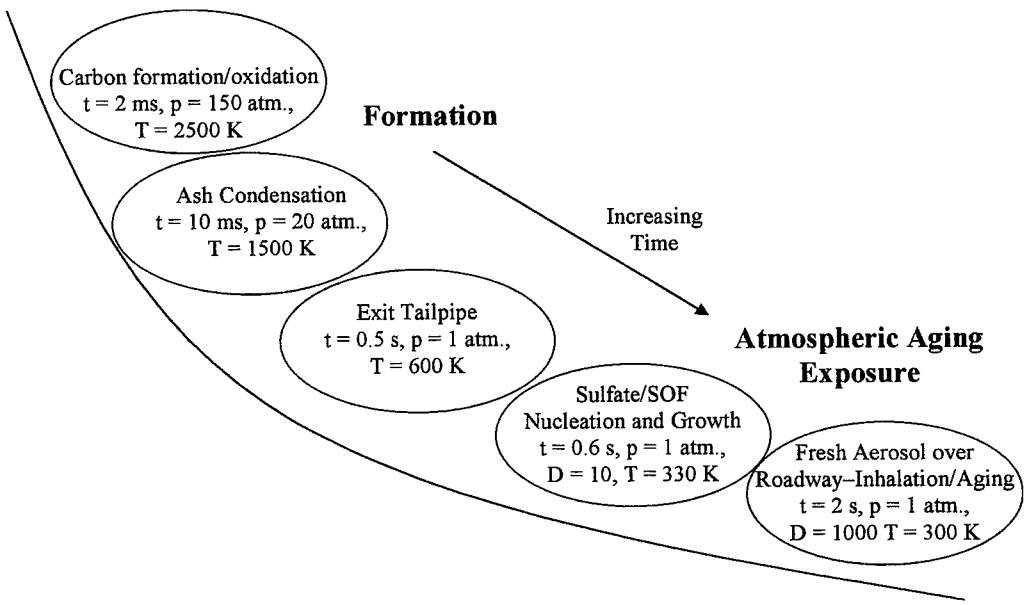
by
Professor David B. Kittelson
Center for Diesel Research
Department of Mechanical Engineering
University of Minnesota

3rd ETH Workshop - Nanoparticle Measurements
Zurich, Switzerland
9-10 August, 1999

Outline

- Sampling Problems
  - Homogeneous
- Growth Rates and Limits
- Comparison with Some Recent Measurements
- Conclusions

Particle Formation History:
From the Start of Combustion to the Nose



University of Minnesota

Significant Gas to Particle Conversion Takes Place as the Exhaust Dilutes and Cools

- More than 90% of the particle number may form through homogeneous nucleation of nanoparticles
- From 5 to more than 50% of the particle mass may form through adsorption, absorption, and nucleation
- These processes are very sensitive to dilution conditions
- We will try to establish a theoretical base for this sensitivity
- Nucleation during dilution plays a key role

Binary Nucleation of H_2SO_4-H_2O May Lead to Nanoparticle Formation during Dilution

The rate of nucleation is extremely nonlinear in acid and water concentrations

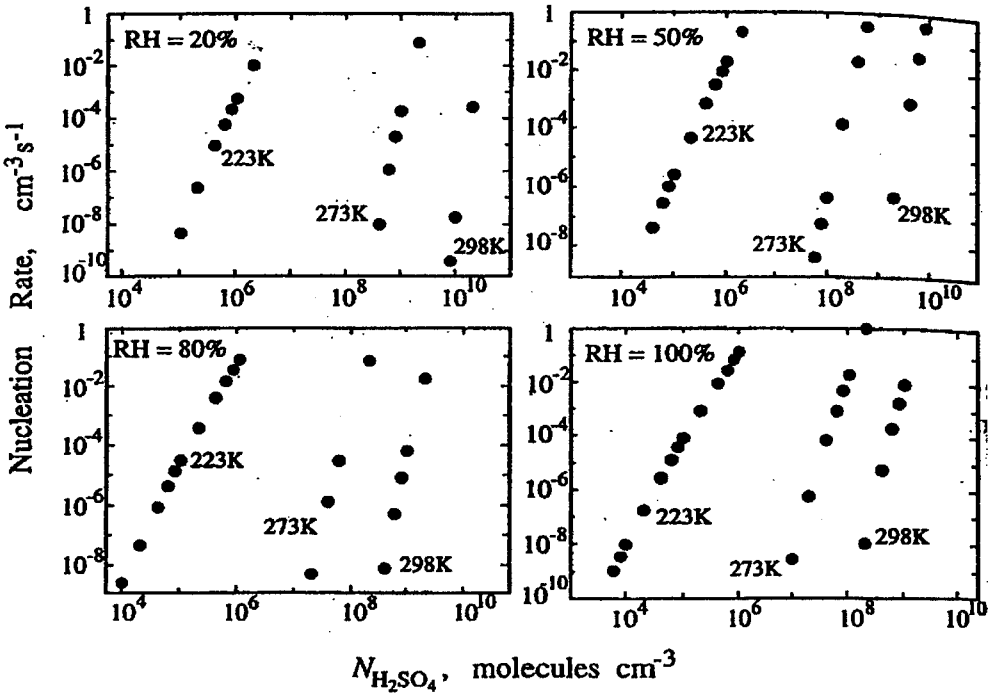


Figure from Seinfeld and Pandis, Atmospheric Chemistry and Physics, 1998

Binary Nucleation of H_2SO_4-H_2O - Empirical Prediction of Nucleation Threshold

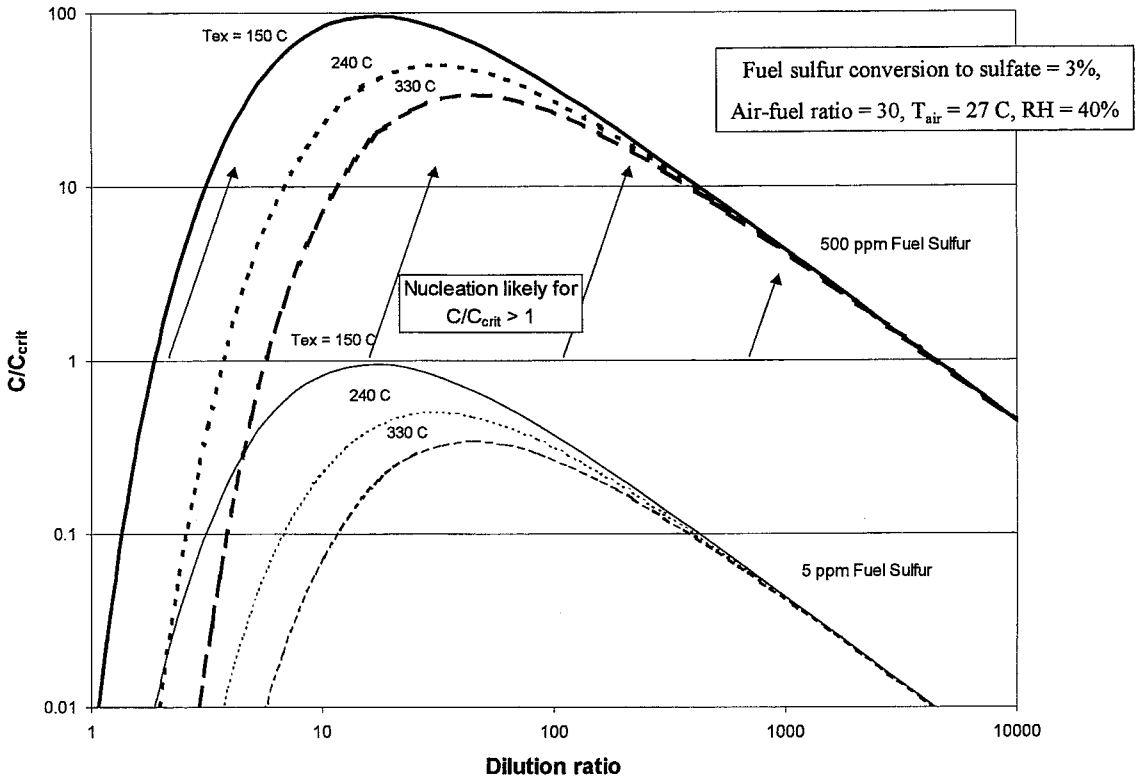
- The extreme dependence of the nucleation rate upon temperature, H_2SO_4, and H_2O concentrations makes theoretical predictions of nucleation difficult.
- Seinfeld and Pandis give an empirical expression to predict the onset of nucleation in this system:

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

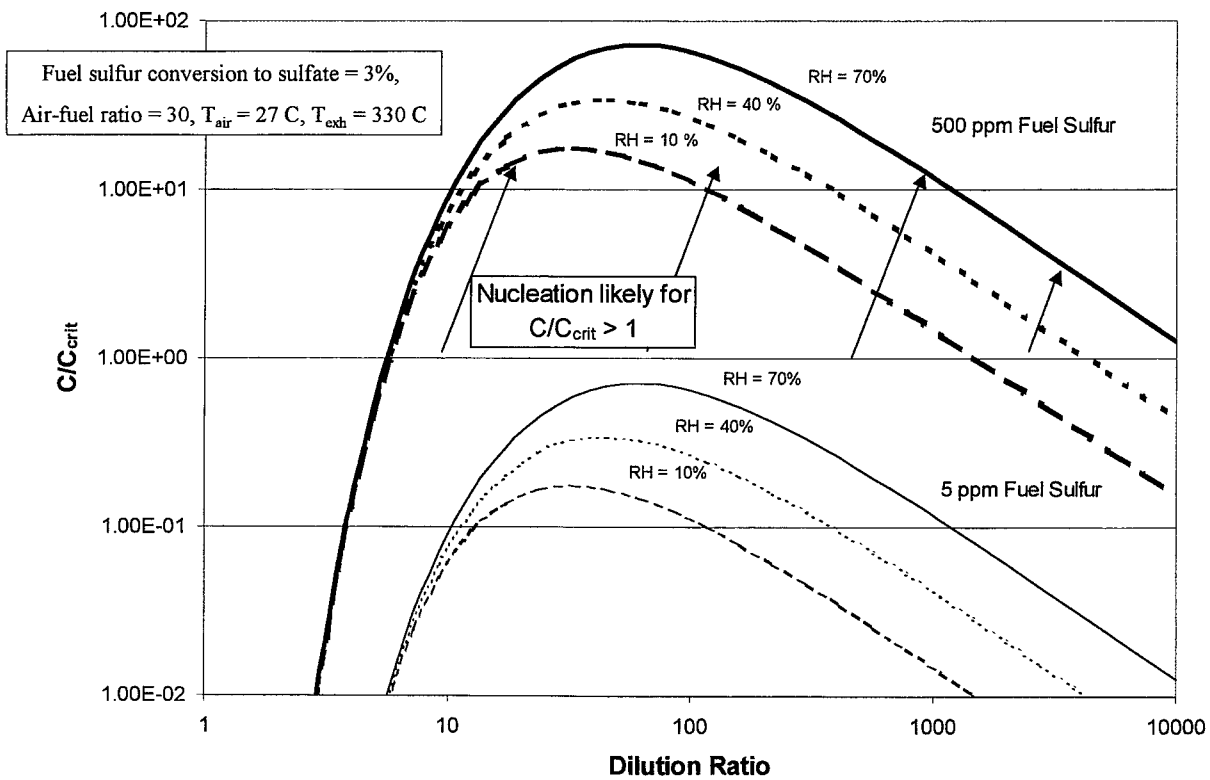
where C_{crit} is the threshold H_2SO_4 concentration in μg/m^3, T is temperature, RH is relative humidity (0 to 1).

- I have used this expression and mass and energy balances applied to the dilution process to predict the ratio of the actual H_2SO_4 concentration to the critical one, C/C_{crit}. When this ratio exceeds one, nucleation is likely.
- The influences of some engine, fuel and sampling conditions on this ratio are shown in the next two slides.

Influence of Fuel Sulfur and Exhaust Conditions on Sulfuric Acid Nucleation



Influence of Fuel and Ambient Humidity on Sulfuric Acid Nucleation



Suppression of Nucleation by Existing Particles

- The presence of adsorbing or absorbing particles may significantly suppress nucleation
- The effectiveness of existing particles in suppressing nucleation depends upon relative rates of vapor adsorption and dilution
- The rate of collision of vapor phase molecules, Z, with particle surface in the free molecular regime is given by:

$$Z = \left(\frac{RT}{2\pi M} \right)^{0.5} A_p N$$

where R is the gas constant, T is temperature, M is molecular mass, A_p is the particle surface area concentration, and N is the concentration of molecules.

Dimensionless Adsorption Rate

- From the expression for Z the time constant for molecular adsorption becomes:

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

- If the variation of dilution ratio with time can be described as:

$$D = 1 + t / \tau_d$$

- A dimensionless adsorption rate can be defined as:

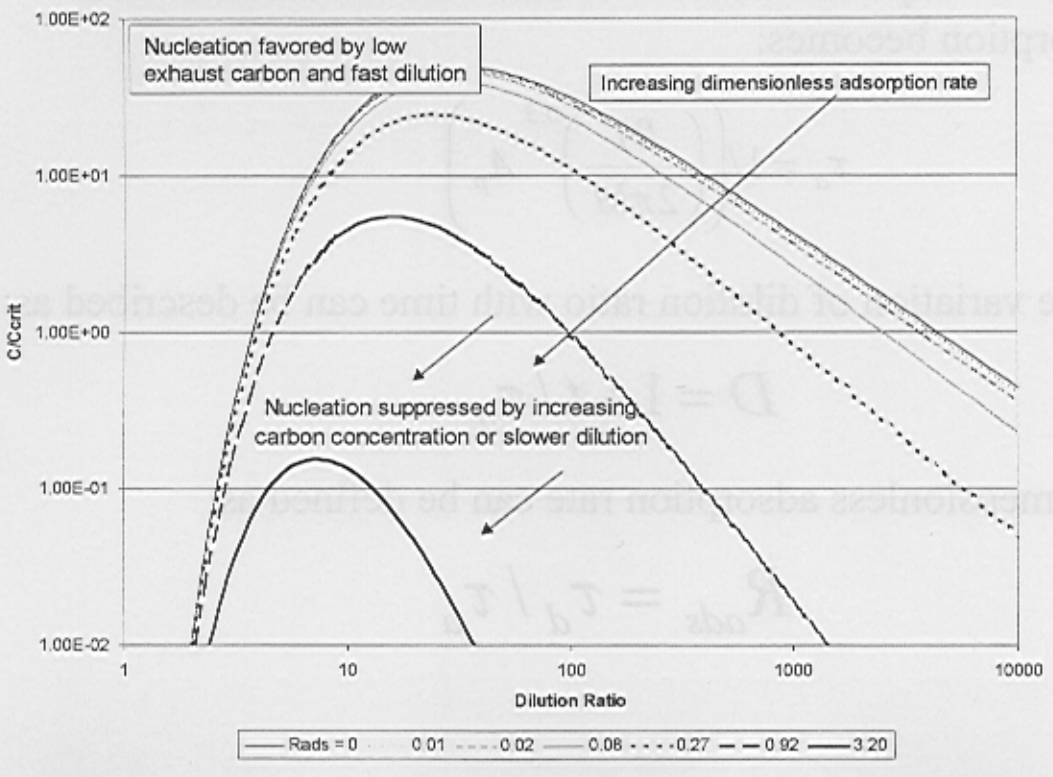
$$R_{ads} = \tau_d / \tau_a$$

Dimensionless adsorption rates, shaded areas indicate significant adsorption, suppression of nucleation.

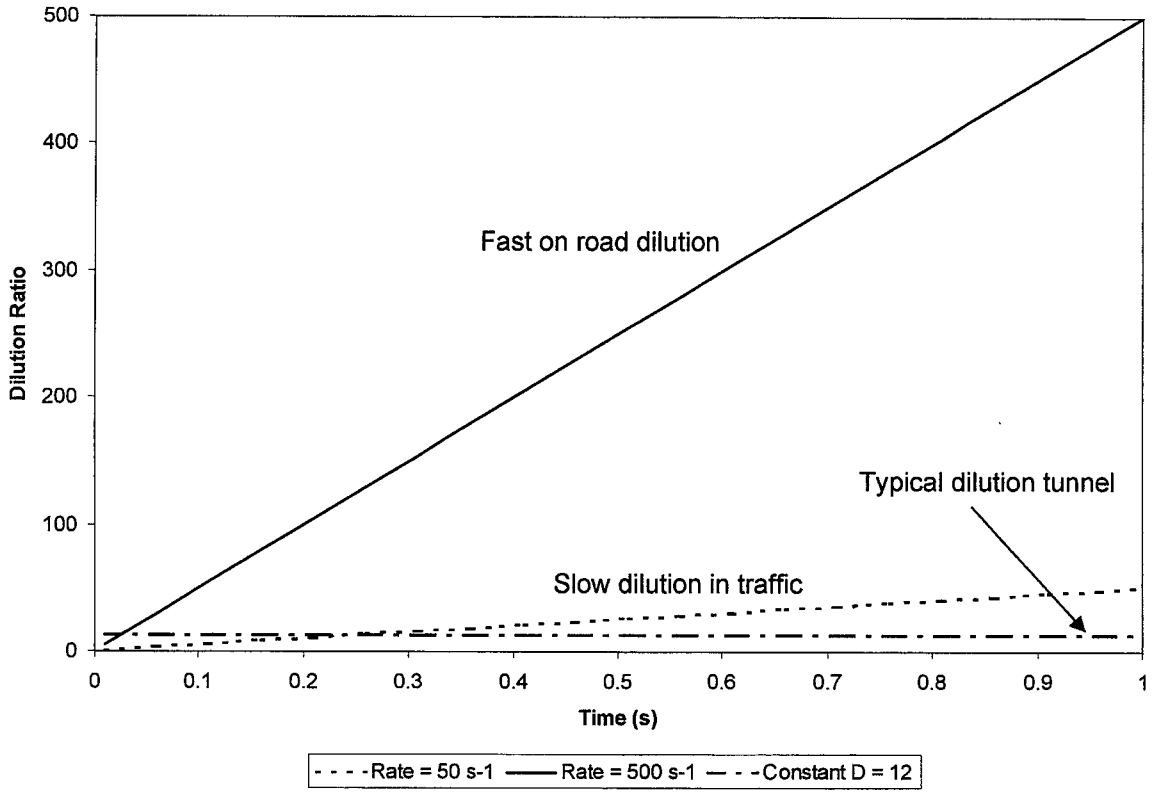
Dimensionless Adsorpion Rate, R_{ads}				
Engine	Exhaust Carbon (mg/m^3)	Dilution rate s^{-1}		
		10	100	1000
Dirty	50	**8**	**0.8**	**0.08**
Current	10	**1.6**	**0.16**	**0.016**
Clean	2	**0.32**	**0.032**	**0.0032**

Assumptions - sulfuric acid adsorption, M = 98, particle specific surface = 25 m^2/gm

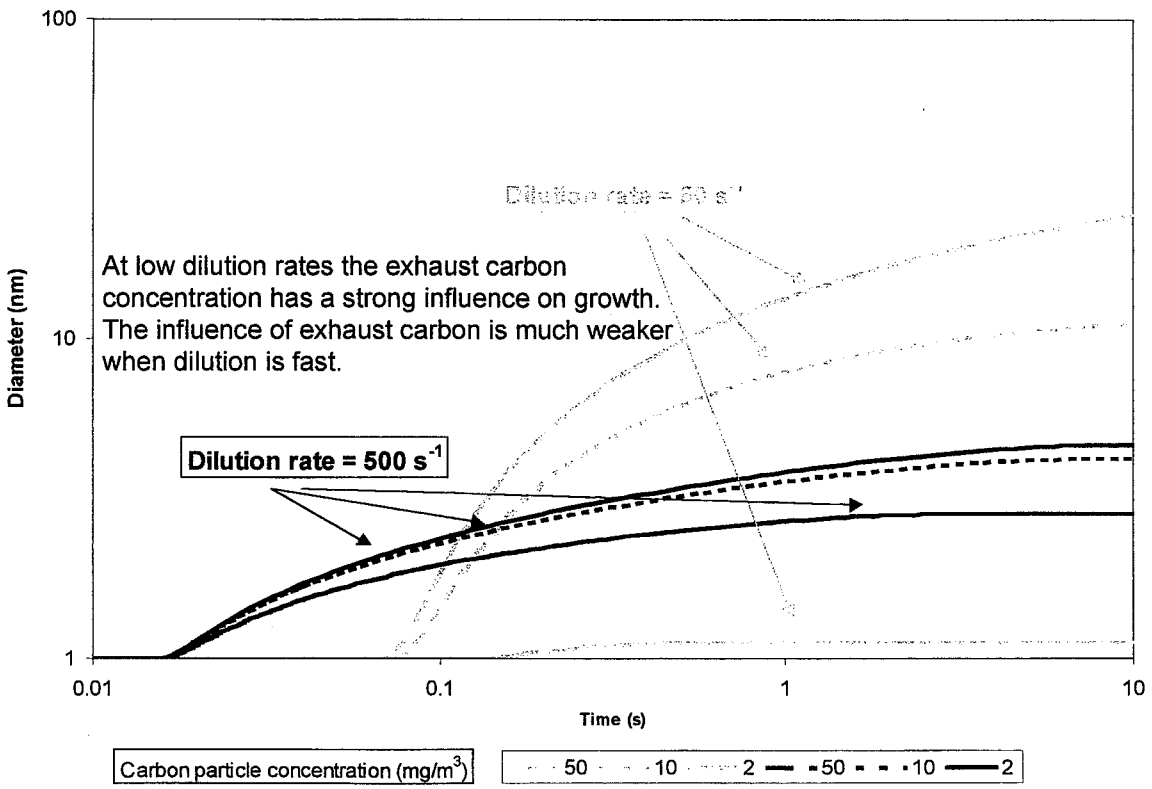
Influence of Dimensionless Adsorption Rate, R_{ads}, on H_2SO_4 Nucleation



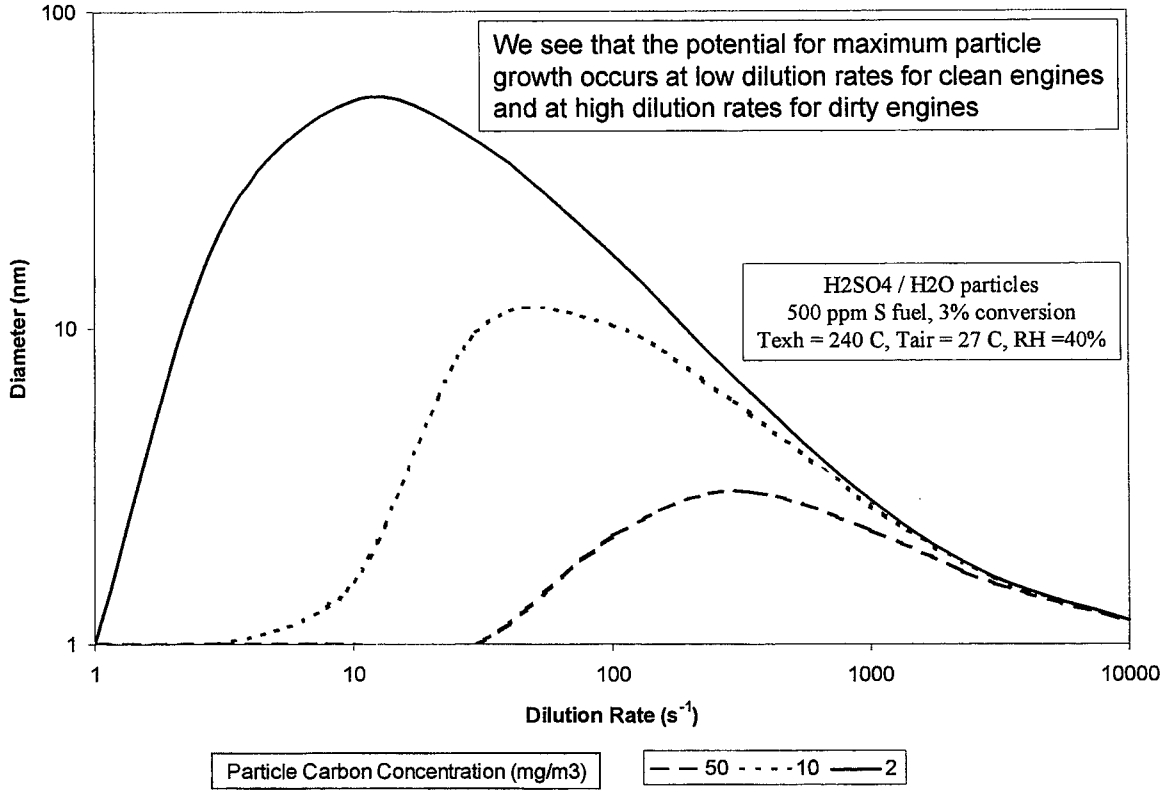
Influence of dilution schedules on growth of nanoparticles - 3 schedules



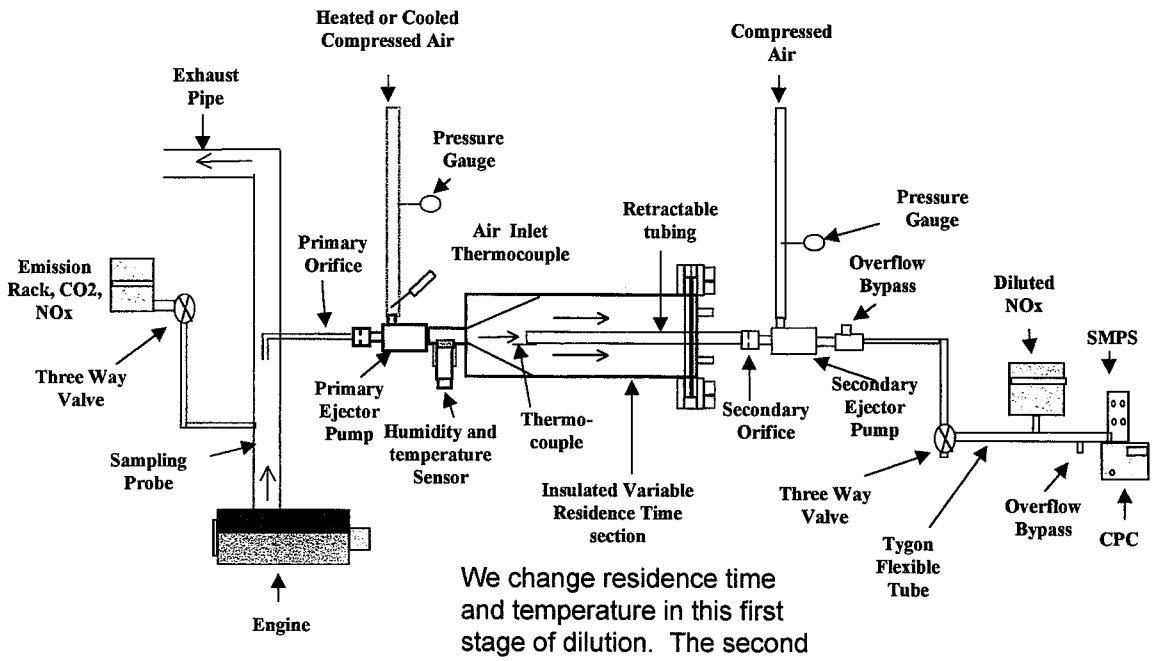
Slow dilution reduces vapor concentrations by adsorption, but allows more time for growth



For each exhaust carbon loading, one dilution rate maximizes nanoparticle growth

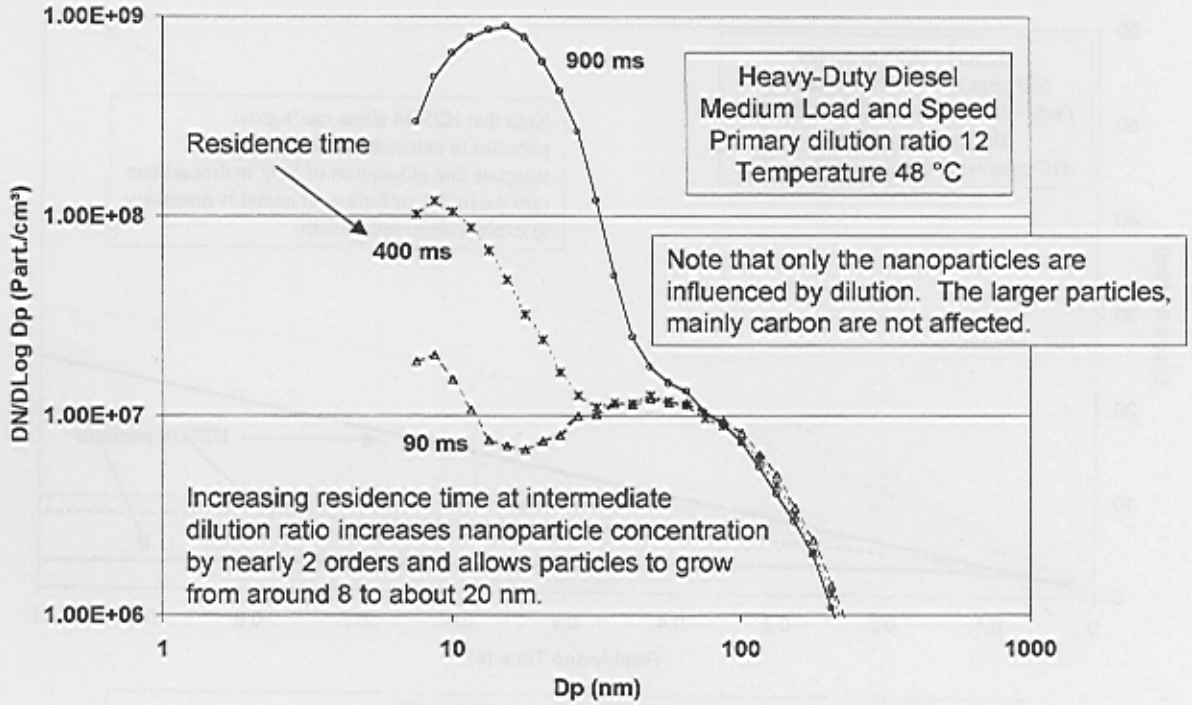


Studies of Nanoparticle Formation Using a Variable Residence Time Dilution System

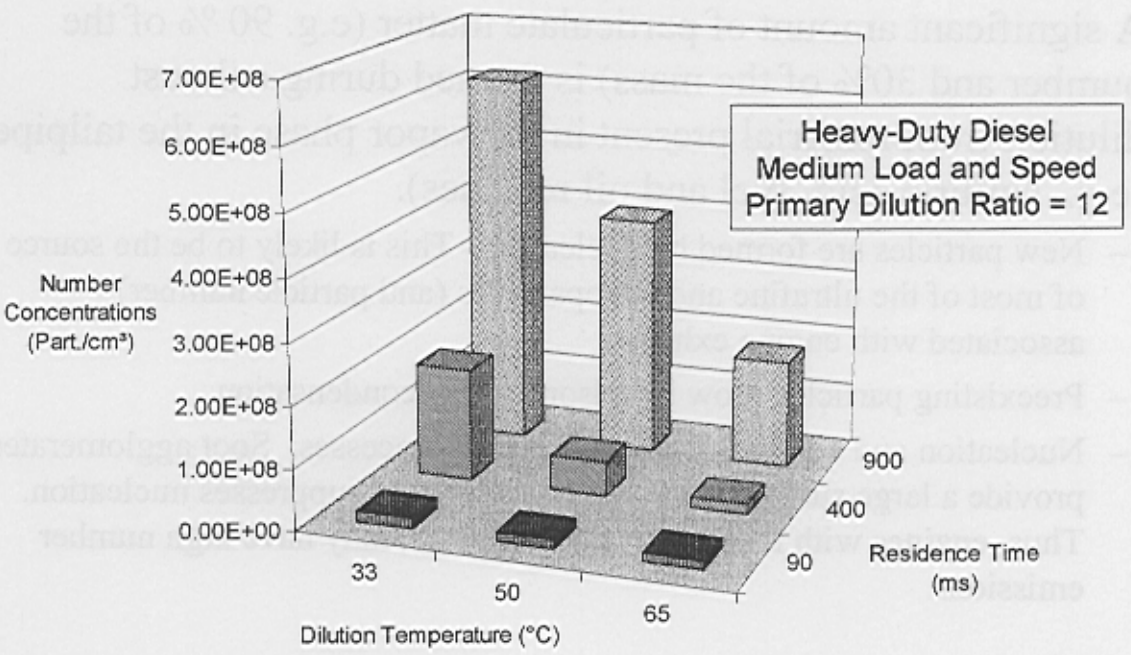


We change residence time and temperature in this first stage of dilution. The second stage freezes formation and growth.

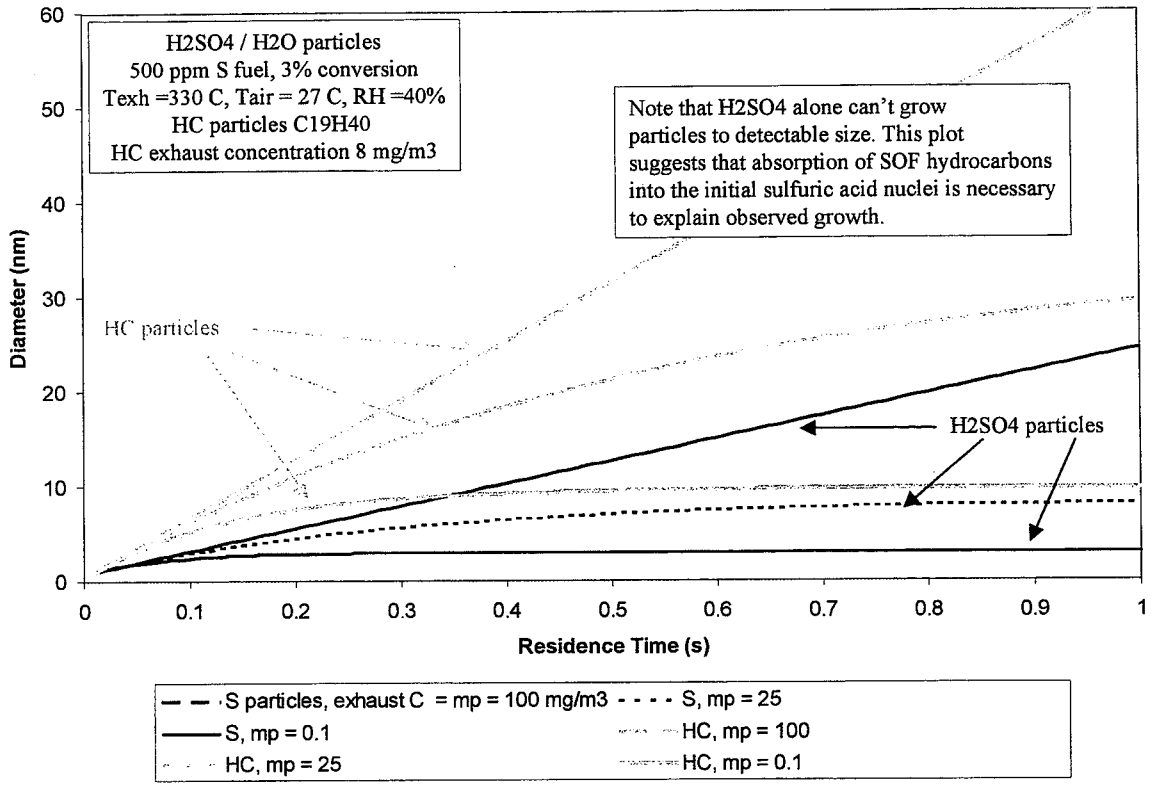
Sensitivity of Particle Size Distribution to Dilution Conditions - Residence Time Effects



Sensitivity of Particle Number Emissions to Dilution Conditions - Residence Time and Temperature Effects



Particle growth at constant dilution ratio of 12, conditions similar to experiments above



Conclusions - 1

- A significant amount of particulate matter (e.g. 90 % of the number and 30% of the mass) is formed during exhaust dilution from material present 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. Soot agglomerates provide a large surface area for adsorption that suppresses nucleation. Thus, engines with low soot mass emissions, may have high number emissions.

Conclusions - 2

- 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 downstream of exhaust filters or with very clean engines where exhaust carbon concentrations are low