Nanoparticle Formation and Evolution in the Exhaust of Vehicles Running on Ultra-low Sulfur fuel

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Abstract

The concern of adverse health impacts from exposure to vehicle emitted nanoparticles (NPs) has been escalating over the past few years. In order to meet more stringent EPA emission standards for NOx and particulate emissions, various combinations of after-treatment systems have to be employed on vehicles. Although they were found to be effective in reducing NOx and particulate emissions, those after-treatments were also revealed to increase the potential of NP formations. The possible causes are 1) enhanced sulfur to sulfuric acid conversion efficiency (ε); 2) sulfur storage/release effect. On the other hand, laboratory studies also measured significant NPs for vehicles without after-treatments running on ultra-low sulfur fuel. The likely reason maybe the presence of nanometer-sized non-volatile cores/particles in NPs.

In this study, a comprehensive modeling work on the effects of the fore-mentioned factors on NP formation and evolution under ultra-low sulfur conditions for vehicles both equipped with/without after-treatments has been carried out. A detailed size- and composition- resolved aerosol microphysical model with a recently improved H_2SO_4-H_2O homogeneous nucleation (BHN) module is applied. We show that model predictions are in good agreement with particle size distributions measured in two recent independent studies.

We find in this study that NP emissions of vehicles running with ultra-low sulfur fuel (FSC~15 ppm) is at least the same, if not higher, than those using high sulfur fuel (FSC~330 ppm) because of employment of DPF or CRT. For vehicles without modern exhaust after-treatments, we show that organics, rather than H_2SO_4, contribute to the growth of non-volatile particles, and even with the size ~ 2 – 3 nm in diameter, they are able to form a clear nucleation mode with mean size larger than 10 nm.

Methods

Formation and evolution of clusters/nanoparticles

$$\frac{\partial C_{i,X}}{\partial t} = l_{i+1,i}\delta_{X,A}\gamma_{i+1,X}C_{i+1,X} - l_{i,i-1}\gamma_{i,X}C_{i,X}$$
$$+\sum_{j=1}^{i}\sum_{k=1}^{i-1} f_{j,k,i}\beta_{j,k}N_j C_{k,X} - C_{i,X}\sum_{j=1}^{i\max}\left(1-f_{i,j,i}\right)\beta_{i,j}N_j$$

Organic condensation scheme

$$\frac{\partial C_{i,org}}{\partial t} = \pi V_{org} f_{corr} N_i r_i^2 \nu_{org}\left(P_{org} - P_{s,org}A_{kelvin}\right)$$

Model Comparisons with Measurements

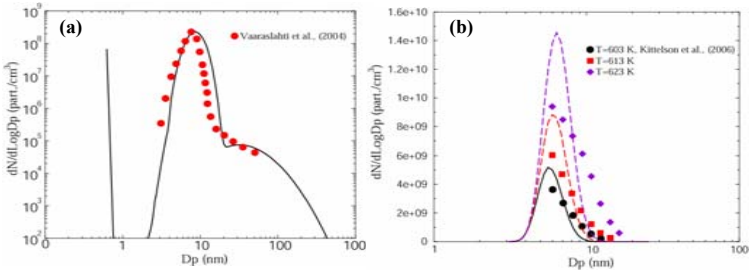

Fig. 1. Predicted particle size distributions and measured ones from (a) Vaaraslahti et al. (2004) and (b) Kittelson et al. (2006). The conversion efficiency ε is assumed to be 53 %, 67 % and 72 % for exhaust temperature of 603 K, 613K and 623 K, respectively. The ε used in Fig. 1 (a) is assumed to be 100 % for exhaust temperature of 750 K.

Effect of Sulfur Conversion Efficiency on NP Formation

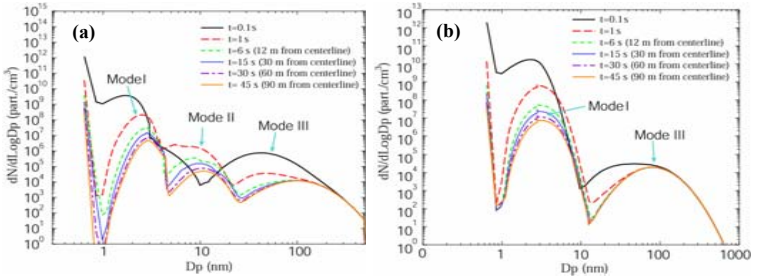

Fig. 2. NP formation and evolution as a function of plume ages up to 75 s under (a) high sulfur conditions (ESC=330 ppm with FSC=330 ppm) and (b) ultra-low sulfur conditions (ESC=30 ppm with FSC=15ppm and LSC=15ppm)in winter condition (T=278 K, RH=60 %). The lube oil sulfur content is assumed to be 3000 ppm and lube oil leaking rate is assumed to be 0.5 %. The conversion efficiency ε is 1.4% for case (a) and 60% for case (b). Dilution is not corrected.

Role of Non-volatile Cores in the Formation of Observed NPs

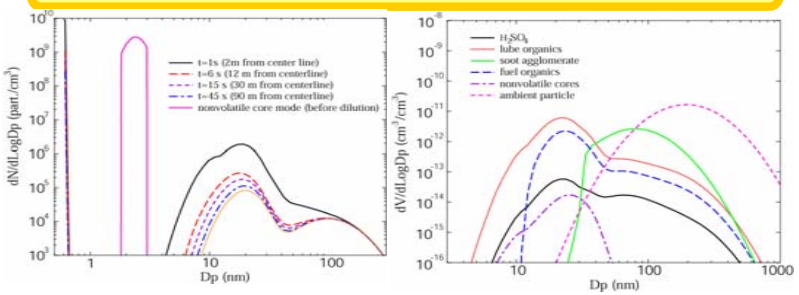

Fig. 4. (a) Number size distributions of NPs at four selected plume ages, and (b) volume size distributions for different components at plume age of 1 s for the case with the presence of refractory particles. The ambient T and RH are 295 K and 60%, respectively. ESC = 50 ppm and ε = 2.5 %.

Effect of Sulfur Release on NP Formation

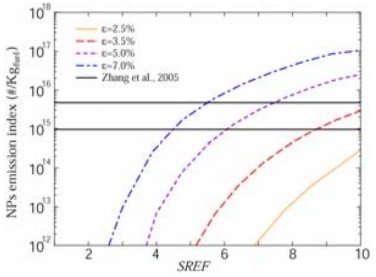

Fig. 3 NP emission indices as function of *SREF* at 4 different ε (2.5 %, 3.5 %, 5.0% and 7.0 %) at ambient *T*=298 K and *RH*=50 %. The ESC is assumed to be 30 ppm.

Conclusion and Discussion

1. We showed from modeling simulations that BHN still is the dominant process in producing NPs for vehicles equipped with new diesel particular filter (DPF) or continuously regenerating trap (CRT) even when fuel sulfur content reduced to 15 ppm.
2. Vehicles equipped with DPF or CRT running on ultra-low sulfur fuel emit at least the same, if not higher, NPs than those without after-treatments using high sulfur fuel (FSC~330 ppm).
3. Sulfur release effect can also lead to enhanced NP formation even when sulfur conversion efficiency is low under ultra-low sulfur conditions.
4. For vehicles without modern after-treatments, a clear nucleation mode with mean size larger than 10 nm can be formed by condensation of sulfuric acid and organic species onto non-volatile cores formed at low engine load inside engine cylinder

Acknowledgements

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References

1. Kittelson, D. B., et al.: On-road evaluation of two Diesel exhaust aftertreatment devices, Journal of Aerosol Science, 37, 1140-1151, 2006.

2. Ronkko, T., Virtanen, A., Kannosto, J., Keskinen, J., Lappi, M. and Pirjola, L. (2007). Nucleation Mode Particles with a Nonvolatile Core in the Exhaust of a Heavy Duty Diesel Vehicle. 41: 6384-6389.

3. Vaaraslahti, K., Keskinen, J., Giechaskiel, B., Solla, A., Murtonen, T. and Vesala, H. (2005). Effect of Lubricant on the Formation of Heavy-Duty Diesel Exhaust Nanoparticles. 39: 8497-8504