

Effect of exhaust after-treatment on characteristics of diesel nucleation mode particles

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The characteristics of the exhaust nucleation mode particles of heavy-duty diesel engine were studied (Lähde et al. 2008). The engine was 440 PS/323 kW 6 cylinder turbo charged common rail engine with EGR and fulfils Euro IV standard if it is equipped with PM-KAT. Engine displacement was 10.5 dm³ and peak torque 220 Nm. Test cycle consisted of four steady-state driving conditions corresponding to ESC modes 3, 10, 11 and 12. Before each cycle, mode 12 was used to warm the engine. The order and durations of each mode periods were kept similar in all tests to ensure the repeatability of test set and comparability of runs with different after-treatment systems (Vaaraslahti et al. 2005).

The particle emission measurements were made at an engine dynamometer without after treatment systems, with oxidation (DOC) catalyst and with diesel particle filter (DPF). The catalyzing material in both DOC and DPF was platinum 40 gram/foot³ and 20 gram/foot³, respectively. Sulphur content of the used fuel (FSC) was 36 ppm. Exhaust sampling and dilution were done with porous tube type diluter followed by residence time chamber and ejector type diluters. Particle size distributions of the diluted sample were measured with Nano-SMPS (TSI Inc.), SMPS (TSI Inc.) and ELPI (Dekati Inc.). Particle volatility characteristics were studied at ESC 12 by using a thermodenuder (Dekati Inc.). Electrical charge of the particles was measured by AIS (Mirme et al., 2007: AIS, AIREL Ltd). The results of AIS measurements are mainly reported in Lähde et al. (2008).

The nucleation mode was observed with all the tested after treatment devices and in various engine load modes. When the engine was used without exhaust after-treatment devices, bimodal

distribution was observed also in the particle volatility measurements made with thermodenuder. The result indicates that the nucleation mode particles consisted non-volatile core and volatile compounds condensed on it and confirms our previous results (Rönkkö et al. 2007). Thus the nucleation mode can exist also when the sulphur content of fuel and lubricant oil and the conversion of SO₂ to SO₃ are low. Similar results were found for DOC. This indicates that the formation of the particles is similar to without exhaust after-treatment. However, when DOC is used, the particle growth can be sulphur dominated, especially at high load conditions.

With DPF, at low load conditions the exhaust particle concentration was close to the detection limit of the particle measurement instruments. Instead, at high load conditions the nucleation mode was observed. Practically all particles were removed by thermodenuder indicating that the nucleation mode particles consist of highly volatile materials. The dependence on engine load and the volatility properties mean that with the DPF the formation process of nucleation mode particles is probably sulphur driven. Therefore, it is dependent on sulphur content of fuel and lubricant oil (Vaaraslahti et al. 2005).

In all, the exhaust after-treatment has significant role in the formation and growth processes of nucleation mode particles but also the properties of fuel and lubricant oil affect the particles.

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References:

Lähde, T., Rönkkö, T., Virtanen, A., Schuck, T., Pirjola, L., Hämeri, K., Kulmala, M, Arnold, F., Rothe, D., Keskinen, J. (2008). Submitted to Environmental Science and Technology.

Mirme, A., et al. (2007) A wide-range multi-channel Air Ion Spectrometer. Boreal Env. Res. 12: 247–264.

Rönkkö, T. et al. (2007). Nucleation mode particles with a nonvolatile core in the exhaust of a heavy duty diesel vehicle. Environmental Science and Technology, 41, 6384-6389.

Vaaraslahti, K. et al. (2005). Effect of lubricant on the formation of heavy-duty diesel exhaust nanoparticles. Environmental Science and Technology, 39, 8497-8504.

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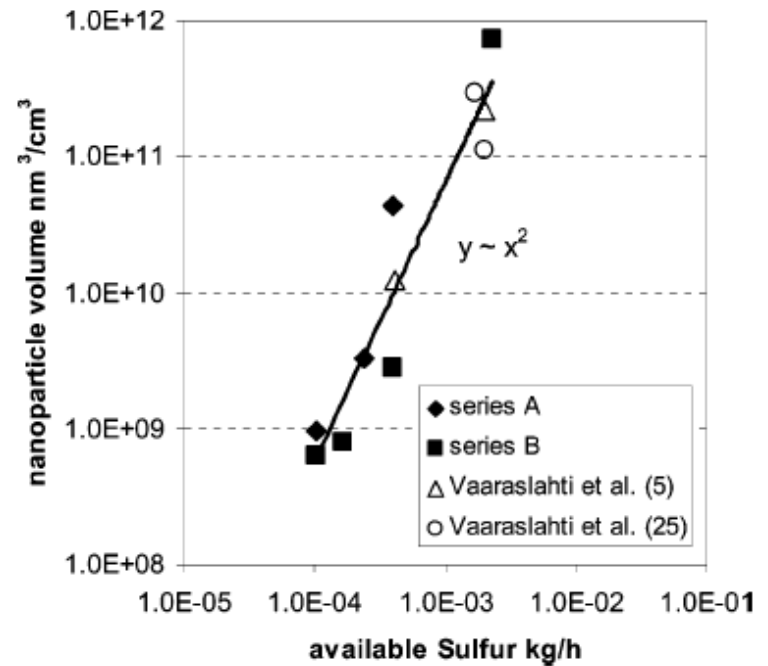
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Background

With diesel particle filter (DPF):

- Sulphur driven nucleation
 - sulphur from fuel and lubricant oil
- Nucleation at high load
 - High temperatures: high SO_2 to SO_3 conversion
- Volatile nucleation mode



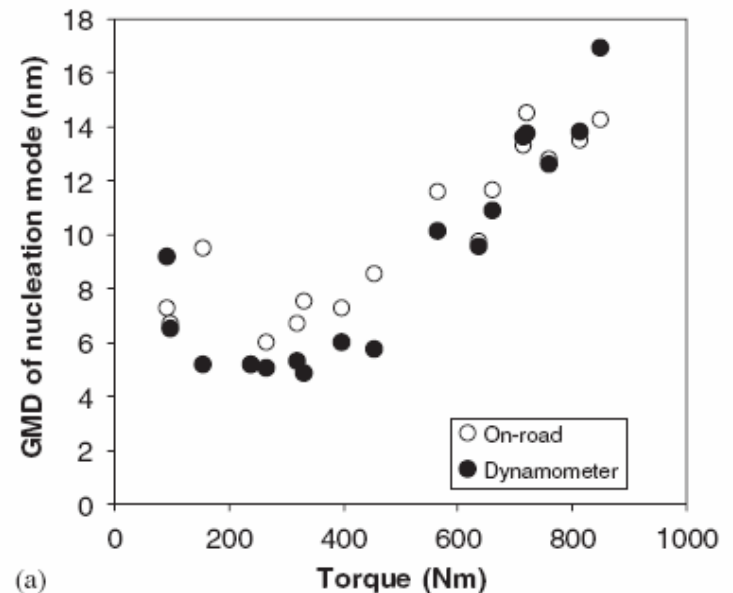
Vaaraslahti et al. 2005



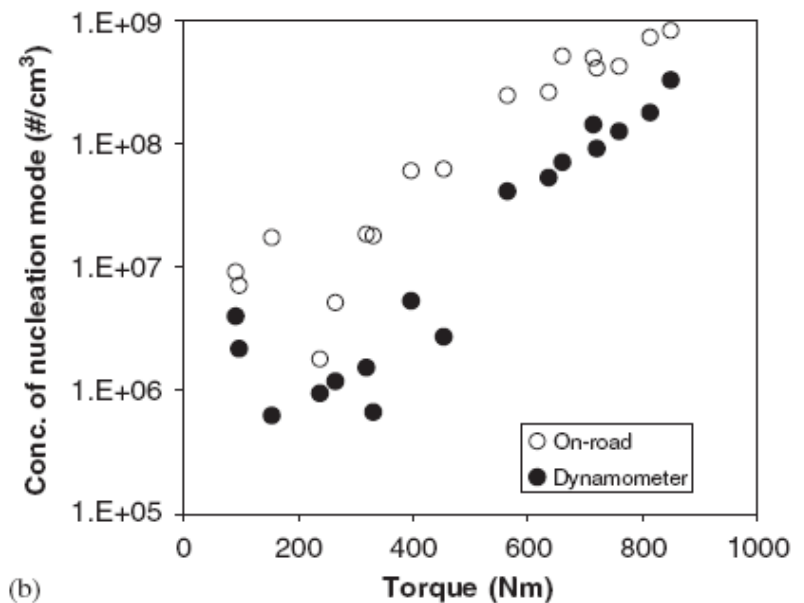
Background

With oxidation catalyst (DOC):
e.g. Rönkkö et al. 2006

- Nucleation mode observed in all tested driving conditions
- Sulphur driven nucleation at high torques, hydrocarbons have role at low torques
- Weak effect of dilution conditions
- Results similar on road and in laboratory



(a)



(b)

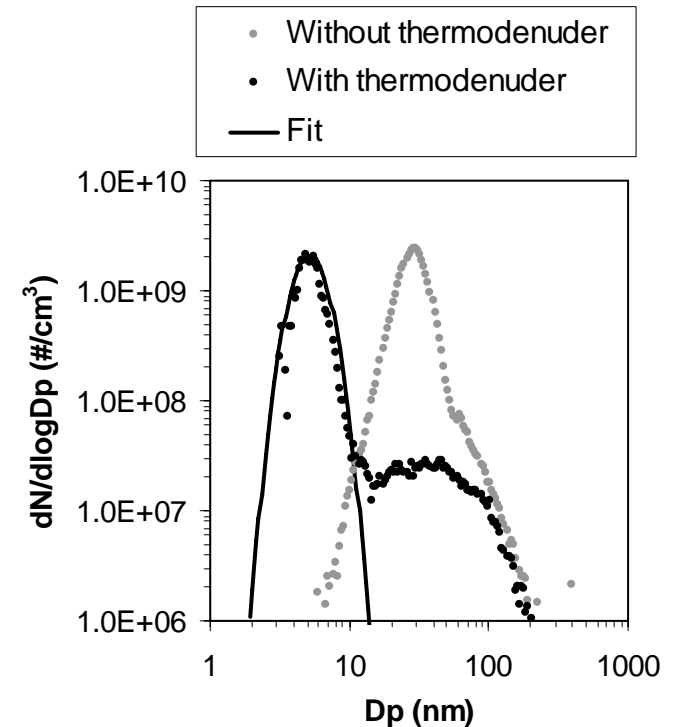


Background

Without after-treatment:

(e.g. Sakurai et al. 2003, Rönkkö et al. 2007)

- No correlation between fuel sulphur and nucleation mode particle number
- Nucleation mode particles consist mostly of hydrocarbons
- Non-volatile core in nucleation mode particles
- Results similar on road and in laboratory
- Dilution conditions do not have significant effect on particle number



Background

Questions to be solved:

- What is the origin of nucleation mode particles
 - Diesel engine without after-treatment
 - With diesel oxidation catalyst (DOC)
- Role of sulphur?



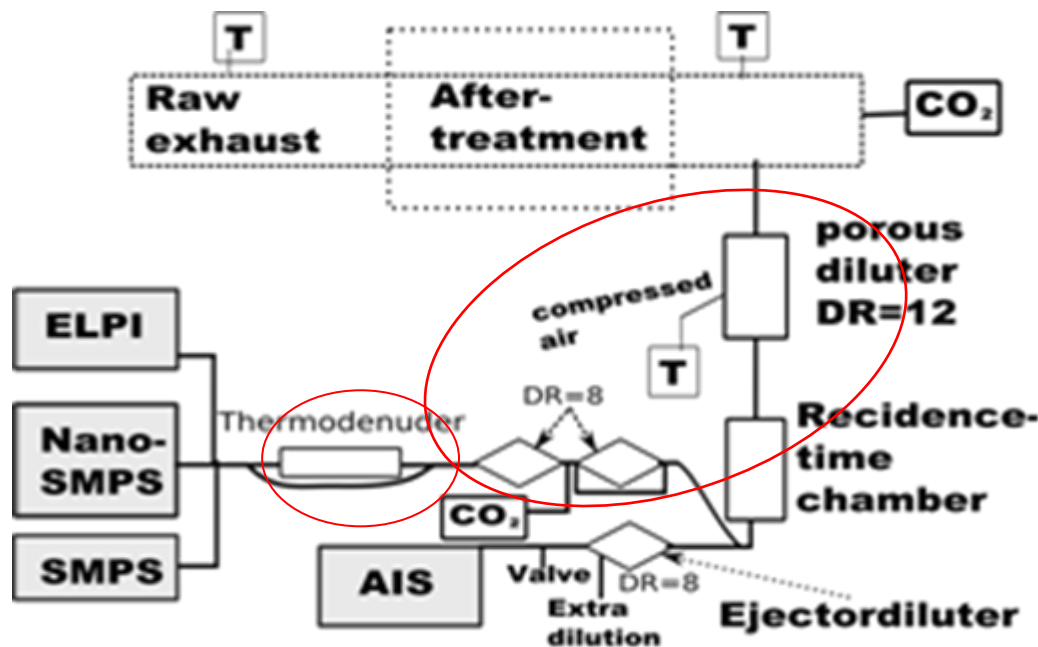
Measurements

Particle sampling

- porous tube diluter
- Ageing chamber
- Ejector type diluter(s)
- Dilution ratio calculated based on CO₂ values

Volatility

- Thermodenuder, particles losses measured



Instruments

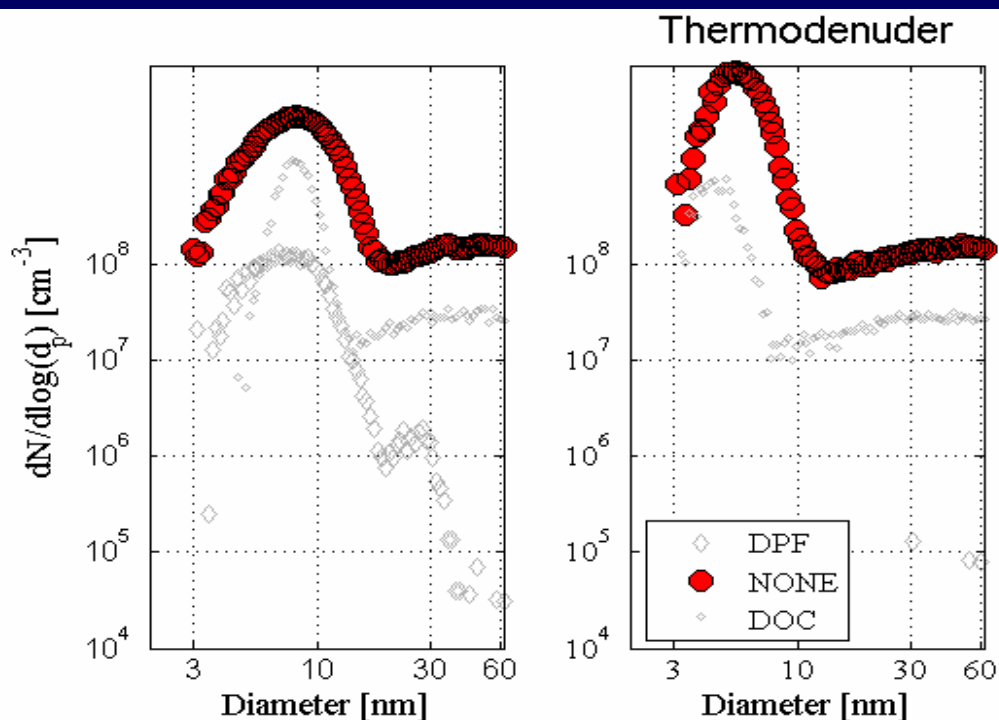
- ELPI
- Nano-SMPS (3-60nm)
- SMPS (10-400nm)
- AIS

Experimental

- Heavy-duty diesel engine (Lähde et al. 2008):
- 440 PS/323 kW, 6 cylinder turbo charged common rail engine with EGR.
- Displacement 10.5 dm³, peak torque 220 Nm.
- Test cycle consisted of warming and four steady-state driving conditions corresponding to ESC modes 3, 10, 11 and 12
- The sulfur content of the fuel (FSC) was 36 ppm.
- Measurements were conducted on engine test bench
 - Without after-treatment
 - With oxidation catalyst (DOC)
 - With coated diesel particle filter (DPF)
- Volatility measurements at 75% load (ESC12)



Results of volatility studies: no after-treatment

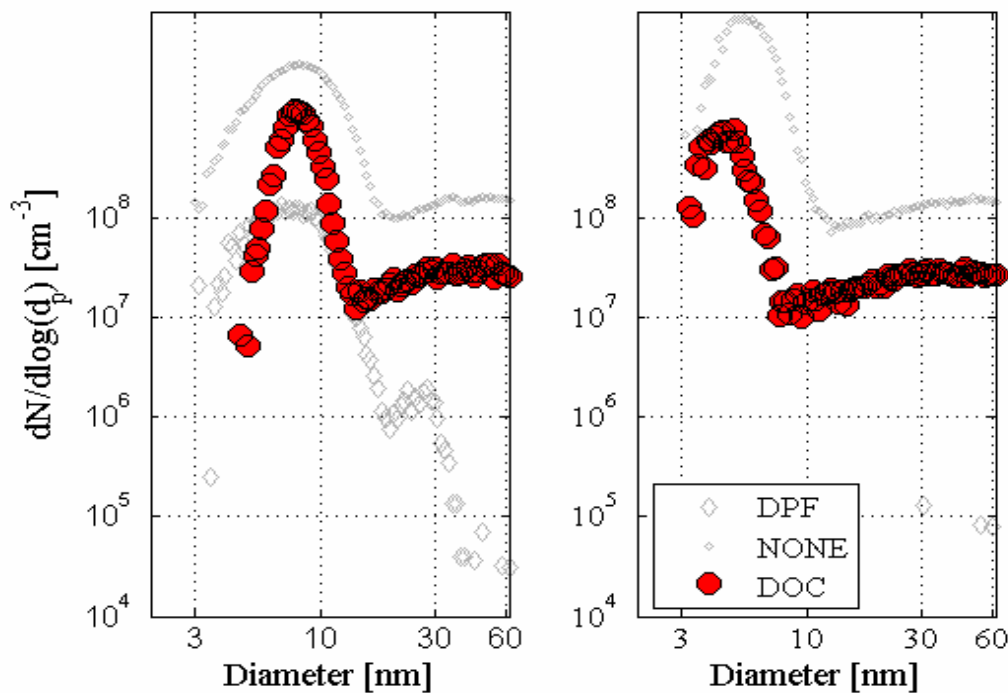


- **Particles have non-volatile core (GMD 5- 7 nm)**
- The core particles are charged (AIS measurement, Lähde et al. 2008)
- Low sulphur, no correlation with sulphur and nucleation mode
- Analysis of Sakurai et al. 2003: volatile material mostly hydrocarbon compounds

→ hydrocarbon growth of solid core particles



Results of volatility studies: DOC

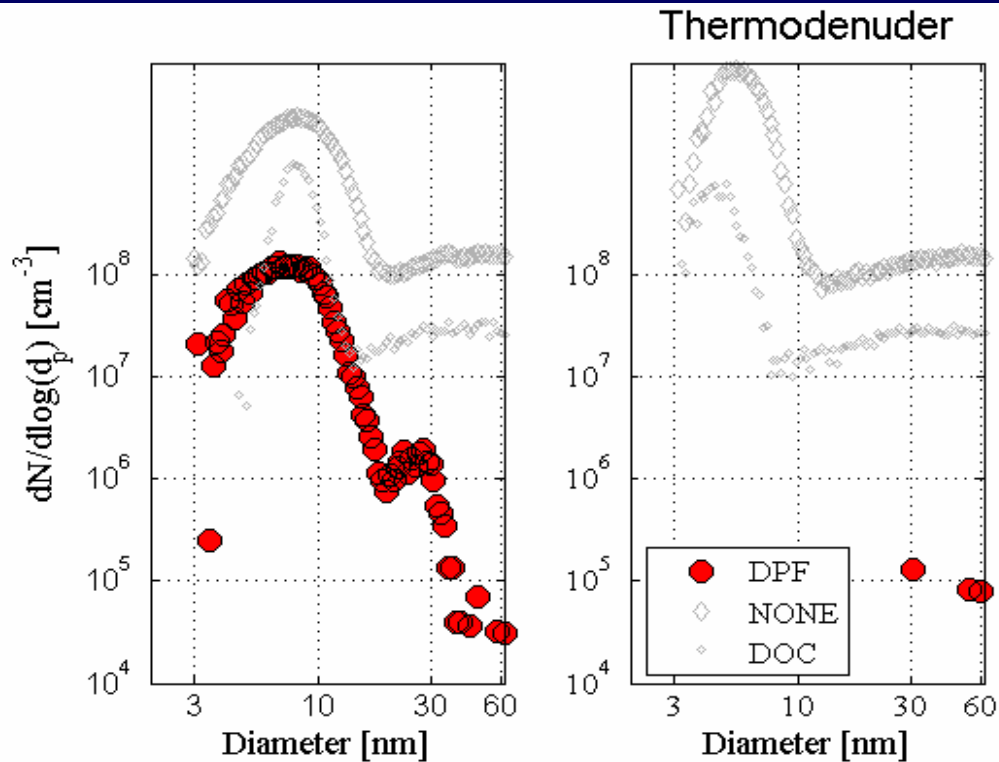


Non-volatile core particles also with DOC

- The core particles are charged (AIS measurement, Lähde et al. 2008)
- Growth by
 - Hydrocarbons (low loads) (e.g. Rönkkö et al., 2006)
 - Sulphur (high loads and/or high FSC)
 - Explains results of Vogt et al (2003) and Schneider et al.



Results of volatility studies: DPF



With DPF only volatile nucleation mode particles

- Nucleation mode only at highest loads
 - conversion of SO₂ to SO₃ is higher
 - Hydrocarbons are removed efficiently

→ Sulphur driven nucleation



Conclusions

Exhaust after-treatment has an effect on

- Existence of nucleation mode
- Existence of non volatile core
 - DPF removes the core particles



Conclusions

Results indicate two different formation mechanisms for nucleation mode particles

- **Non-volatile core particles formed before dilution**
 - **Without after-treatment**
 - Growth dominated by hydrocarbon compounds
 - **With DOC**
 - High loads: growth dominated by sulphur
 - Low loads: growth dominated by hydrocarbons
- **Volatile nucleation mode particles**
 - **With DPF**
 - Nucleation during dilution and cooling
 - Sulphur driven
- **Mixed cases possible**
 - **With DOC and/or high sulphur**



References

- Lähde, T. et al. (2008). Submitted to *Environ. Sci. Tech.*
- Rönkkö, T. et al. (2006). Effect of dilution conditions and driving parameters on nucleation mode particles in diesel exhaust: laboratory and on-road study. *Atmos. Environ.*, **40**, 2893-2901.
- Rönkkö, T. et al. (2007). Nucleation mode particles with a nonvolatile core in the exhaust of a heavy duty diesel vehicle. *Environ. Sci. Tech.*, **41**, 6384-6389.
- Sakurai, H. et al. (2003) Size dependent mixing characteristics of volatile and nonvolatile components in diesel exhaust particles. *Environ. Sci. Tech.*, **37**, 5487-5495.
- Schneider, J. (2005) Nucleation particles in diesel exhaust: composition inferred from in situ mass spectrometry analysis. *Environ. Sci. Tech.*, **39**, 6153-6161.
- Vogt, R. et al. (2003) On-road measurement of particle emissions in the exhaust plume of a diesel passenger car. *Environ. Sci. Tech.*, **37**, 4070-4076.
- Vaaraslahti, K. et al. (2005). Effect of lubricant on the formation of heavy-duty diesel exhaust nanoparticles. *Environ. Sci. Tech.*, **39**, 8497-8504.

