H. Lüders
FEV Motorentechnik GmbH & Co. KG
Aachen

Effect of Measurement Conditions on Ultrafine Particle Emissions

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Hartmut Lüders
FEV Motorentechnik GmbH & Co. KG, Aachen

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1. Introduction

Due to it´s high thermal efficiency the diesel engine has a unique position with respect to lowest fuel consumption and CO_2-emission. However the big disadvantage of the diesel engine is it´s particulate emission. Since basic investigations have shown that a health risk for humans caused by diesel particles probably can't be excluded [1], the particulate emission of diesel engines has been the main topic of many environmental discussions.

For this reason the important industrial nations of the world have defined special exhaust regulations in order to limit the mass related particulate emission of diesel engines. However, considering the latest results of special health studies, it is questionable, whether the emitted particulate mass is a suitable measure for the health risk of diesel particulates. There are indications that other particle characteristics like size or surface could be more important for the toxicological, mutagenious or cancerogenious impact of diesel particles rather than the particulate mass itself [2,3,4,5]. Thus the question of how particulate mass reducing measures do influence the non mass related particulate characteristics gains more and more importance.

FEV has been working on particulate size distribution measurements for many year. In this time a number of programs with different objectives have been carried out, Figure 1. Cooperations with well-known expert groups have been established, Figure 2.

Objectives / Programs in Particle Sizing

Programs at FEV To Date:

- PSD from diesel engines (passenger car to HD engines, steady-state and transient)
- PSD from gasoline engines
- Effect of diesel exhaust gas aftertreatment on PSD
- Effect of fuel composition on PSD
- Fundamental investigations on the chemical and physical nature of ultrafine particles
- Investigations on the effect of particle formation downstream aftertreament systems
- Study of parameters affecting ultrafine particle formation

Ongoing / Forthcoming Programs at FEV:

- Effect of combustion system improvement on PSD (e.g. high pressure injection....)
- PSD from DI gasoline engines

FIGURE 1: Programs (+ Objectives) carried out at FEV

Cooperations

- Institute of Applied Thermodynamics (LAT) of RWTH Aachen
- DWI of RWTH Aachen (Surface Analysis)
- Fraunhofer Institute of Toxicology and Aerosol Research (ITA) , Hannover
- Institute for Combustion Technology and Gas Dynamics of Gerhard-Mercator University, Duisburg

FIGURE 2: Cooperations of FEV

End of 1996 a program focussing on the effect of diesel exhaust gas aftertreatement on particle number emissions has been completed. Again, the starting point was that it had been reported frequently that modern aftertreatement systems like diesel oxidation catalysts (DOC) and and diesel particulate filter (DPF) can increase ultrafine particle number although they significantly reduce the total particulate mass emitted. These effects are indeed not new - they have been described already 15 years ago. Such effects would be very important for the assessment of diesel aftertreatment systems.

Further investigations were carried out to study the effect of particle formation downstream DOC and DPF more in detail. First tests were carried out on a passenger car with a TDI diesel engine. The vehicle was operated on steady-state conditions on a chassis dynamometer. Particle size distribution was measured with a Differential Mobility Analyzer (DMA), described in [6]. Samples were taken from a full flow dilution tunnel. The results of these measurements are shown in Figure 3 and Figure 4.

Effect of a Diesel Oxidation Catalyst on Particle Size Distribution

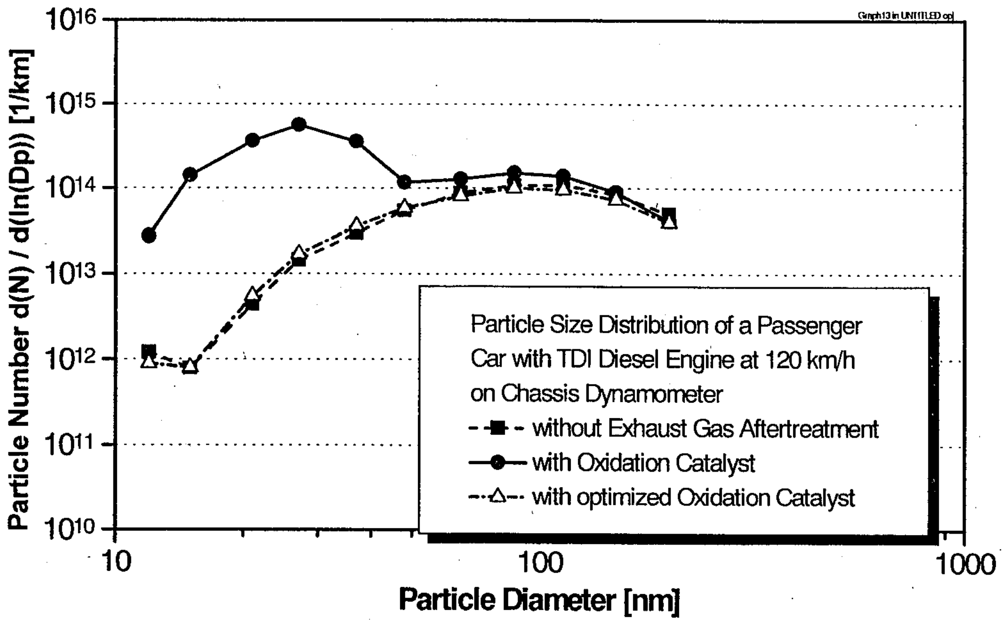

FIGURE 3: Effect of a Diesel Oxidation Catalyst on Particle Size Distribution

Effect of a Diesel Particulate Filter on Particle Size Distribution

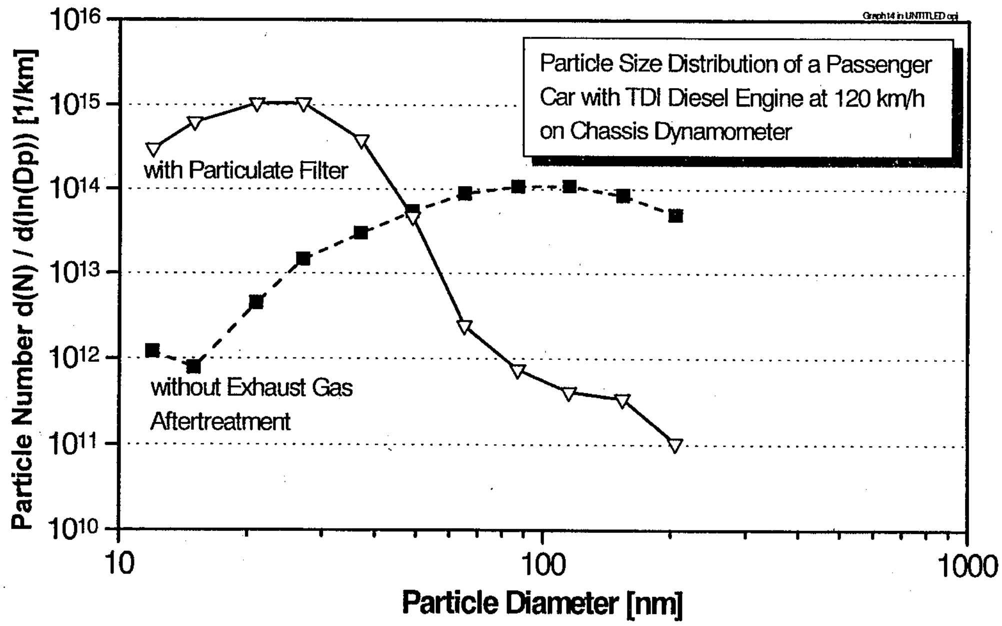

FIGURE 4: Effect on a Diesel Particulate Filter on Particle Size Distribution

Figure 3 illustrates the effect of a diesel oxidation catalyst on particle size distribution with the particle diameter on the abszissa and the particle number on the ordinate. Both axes are of logarithmic scale. Without any aftertreatment a typical size distribution was found. When an oxidation catalyst was used a hugh increase in particle number was found for particles smaller than roughly 50 nm in mean diameter. The number of greater particles was not affected. Afterwards a catalyst with a formulation optimized with regrad to low sulfate formation was used. Then, the particle size distribution was essentially similar to the raw emission (without aftertreatment). From this results it can be conclude that the ultrafine particles formed when a catalyst is used consist of sulfates.

The effect of a diesel particulate filter on particle size distribution is shown in Figure 4. The number of particles greater than roughly 50 nm in mean diameter was substantially reduced by the filter. However, an increase of ultrafine particle was measured again.

The main questionaire that followed from these results is summarized in Figure 5.

Questionaire

Is it possible that Diesel Oxidation Catalysts (DOC) and Diesel Particulate Filter (DPF) act as "reactors" that produce ultrafine solid particles?

What is the nature of the ultrafine particles formed downstream DOC and DPF?

What are the mechanisms that cause ultrafine particle formation?

What is the role of boundary (measuring) conditions?

Is it possible that the ultrafine particles formed downstream DOC and DPF are product of inadequate measuring conditions?

FIGURE 5: Questionaire

Pretty early in that program it got evident that boundary conditions may play a very important role. Usually particle size distribution is measured under the same conditions like total particulate matter, which means that samples are taken from the dilution tunnel. Therefore one might ask: does dilution play a role? Years ago it was already shown in another program that the dilution ratio affects the total particulate matter because of adsorbtion and condensation effects.

Tests to investigate these effects were carried out on a heavy duty diesel engine on a steady-state test bench. The test bench was set-up to provide possibilities to change dilution parameters. When no aftertreament system was used the effect of dilution ratio on particle size distribution was not significant, Figure 6. The dilution ratio given in the figure is the tunnel dilution ratio.

Effect of Dilution Ratio on Particle Size Distribution from a HD Diesel Engine (Raw Exhaust)

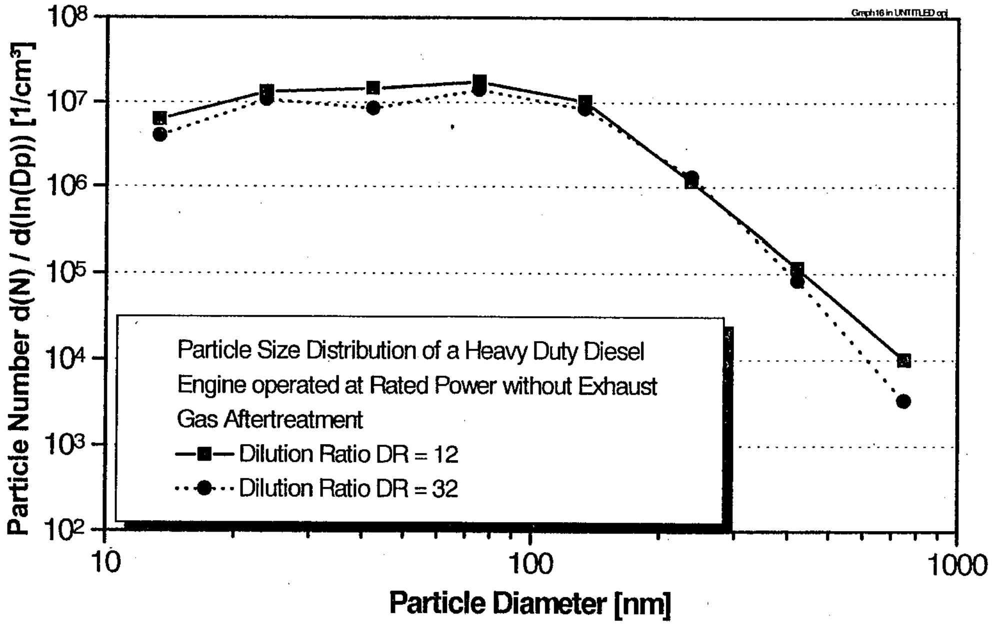

FIGURE 6: Effect of Dilution Ratio on Particle Size Distribution w/o Aftertreatment

Effect of Dilution Ratio on Particle Size Distribution from a HD Diesel Engine with Exh. Gas Aftertreatment

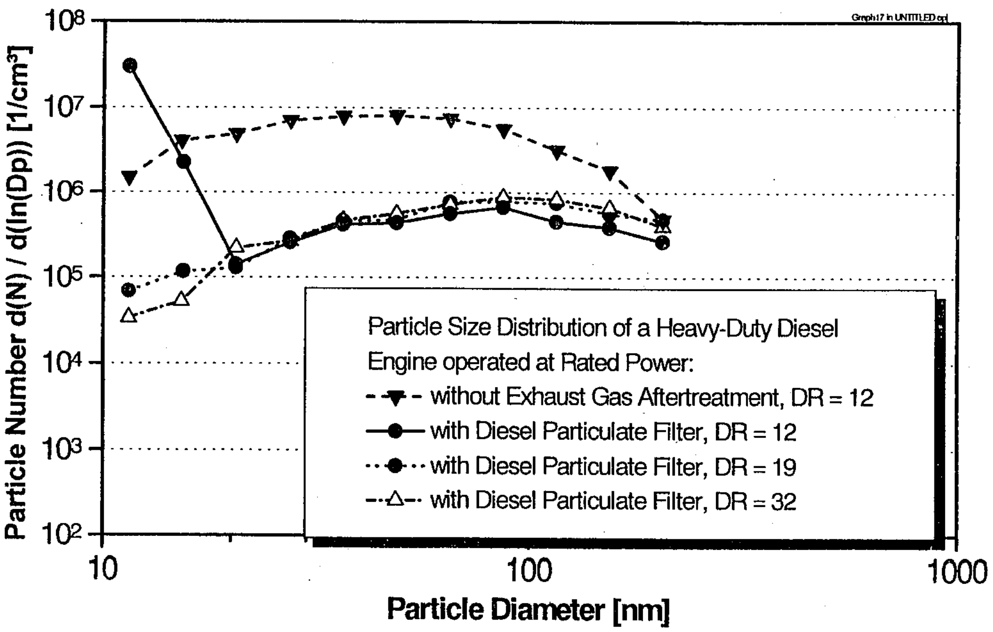

FIGURE 7: Effect of Dilution Ratio on Particle Size Distribution with DPF

When a DPF was installed, however, a significant effect of the dilution was significant, see Figure 7. At a low dilution ratio the typical increase of ultrafine particles was measured again. When the dilution ratio was increased to 19, however, no increase of ultrafine particles was measured. A further increase did not affect particle size distribution. Number emissions of particles greater than roughly 20 nm in mean diameter was not affect by the dilution ratio. From these results it can be concluded that ultrafine particles are formed downstream the DPF because of condensation provoked by very low dilution ratios. Dilution ratio affects mixing temperature, partial pressure and, thus, the concentration of condensation nuclei. At low dilution ratios e.g. the concentration of condensation nucleis may become that high that stable clusters are formed and droplets are formed.

Usually the problem occurs that it is not possible to vary dilution parameters indepentendly. Especially the dilution air temperature is usually "out of control". At FEV a system was set up so that dilution ratio and dilution air temperature can be changed independently. Figure 8 illustrates the effect of dilution air temperature on particle size distribution. At a dilution air temperature of 20 °C ultrafine particles are formed already at a dilution ratio of 12. At higher dilution air temperatures ultrafine particles are not formed at this dilution ratio. Then the dilution ratio was to reduce to 4 in order to provoke ultrafine particle formation.

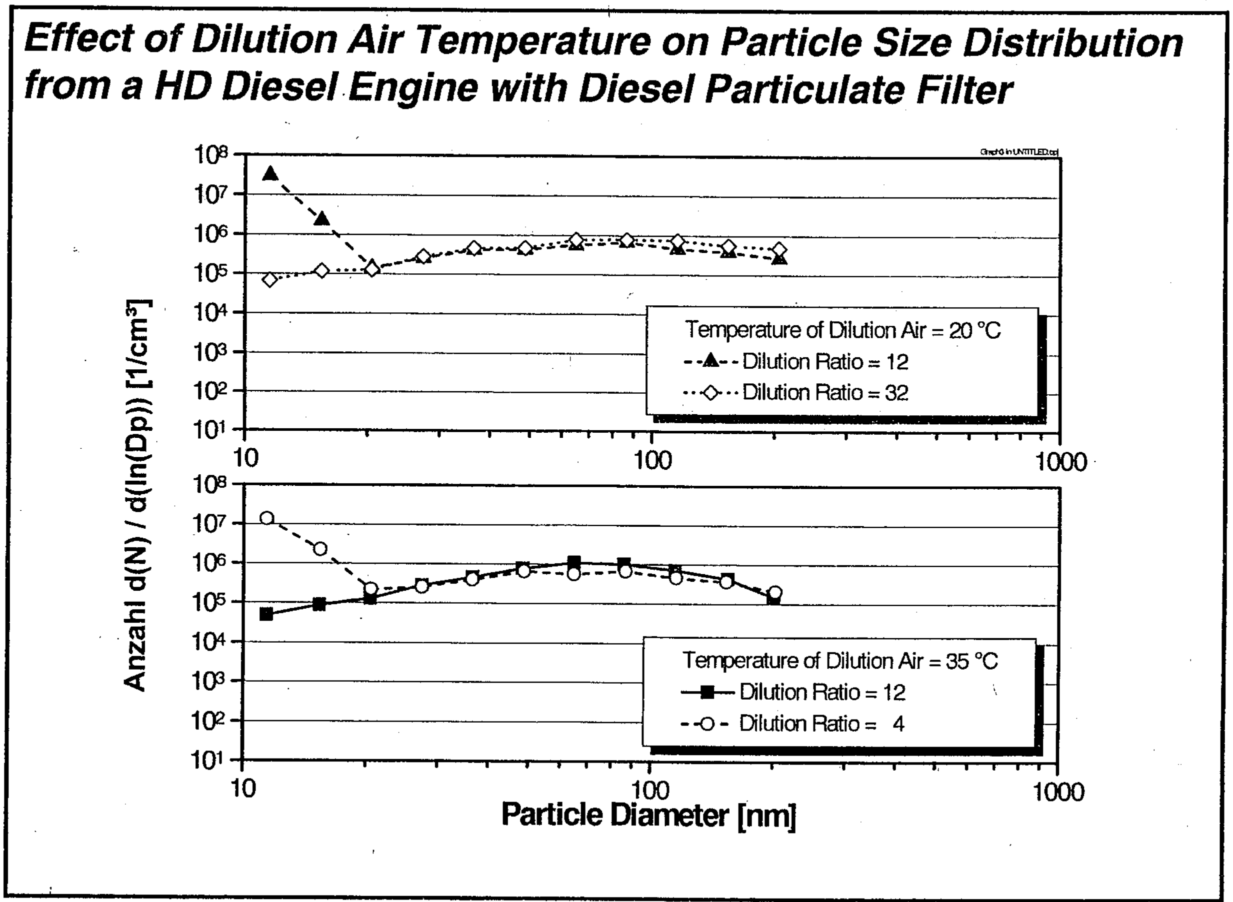

FIGURE 8: Effect of Dilution Air Temperature on Particle Size Distribution downstream DPF

These results also imply that ultrafine particle formation downstream diesel particulate filters and diesel oxidation catalyst is due to condensation effects. This would mean that the particles formed downstream DPF and DOC have no solid core.

Physical Character of Ultrafine Particles formed downstream Aftertreatment Devices

Although the results from the tests mentioned above imply that the ultrafine particled formed downstream aftertreatment devices are product of condensation and do not have a solid core, further test were performed to identify the physical character of these particles more in detail.

There were many approaches to identify the nature of ultrafine particles. However, usually one faces the problem to collect a number / mass of this fraction to analyse it. For this reason an *in-situ* thermogram system consisting of two DMAs and a special heating system was set up. For these tests special analyzers measuring in a very small size range were used. As can be seen in Figure 9 and Figure 10 the particles formed downstream DOC and DPF are evaporized already at 175 °C. From this it can be concluded that these particles can not have a carbonaceous solid core because carbon oxidizes at temperatures significantly higher! This was indeed a very important finding.

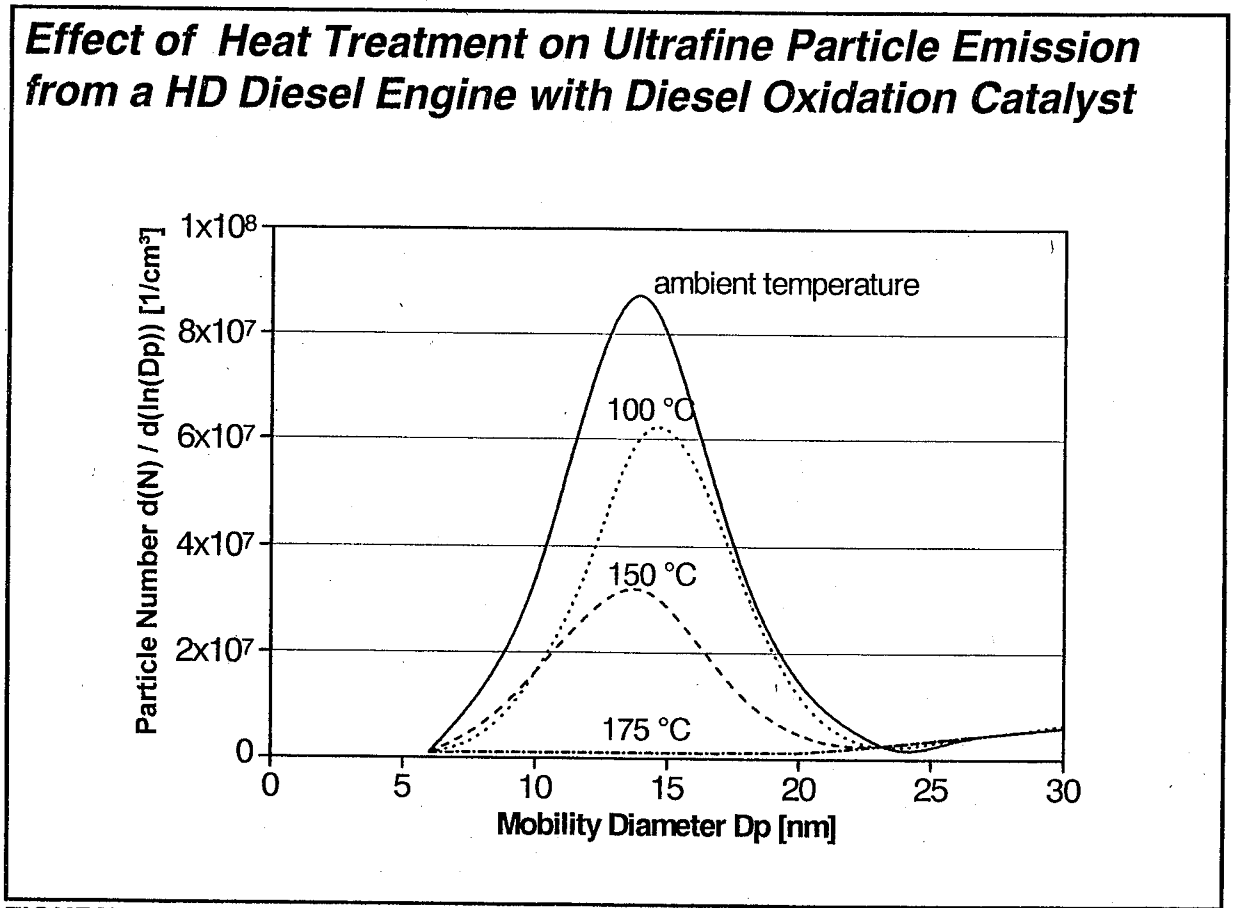

FIGURE 9: Effect of Heat Treatment on Particle Size Distribution downstream a DOC

Effect of Heat Treatment on Ultrafine Particle Emission from a HD Diesel Engine with Diesel Particulate Filter

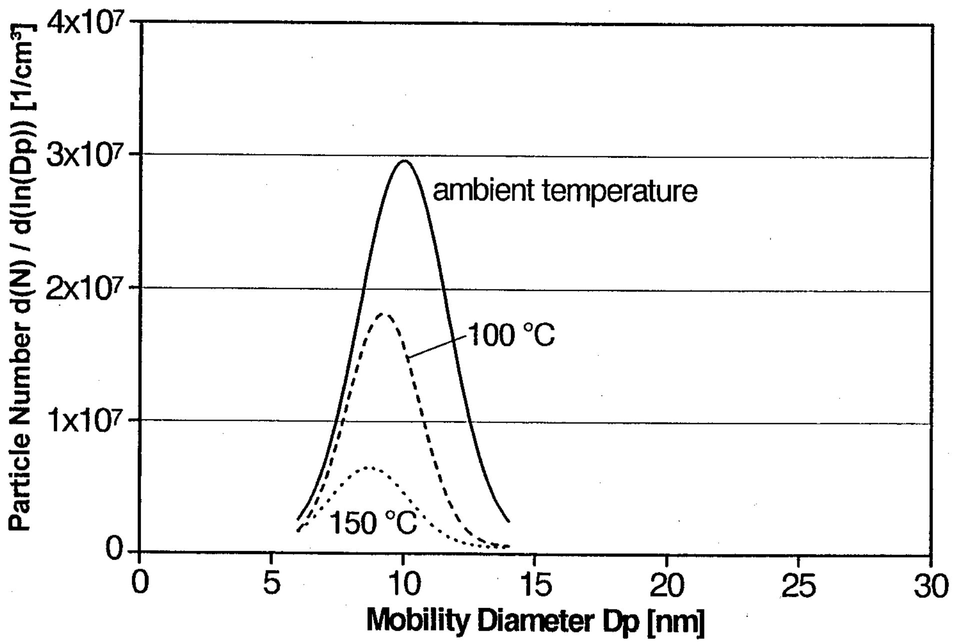

FIGURE 10: Effect of Heat Treatment on Particle Size Distribution downstream a DPF

Summary

Figure 11 summarizes the main results of the program.

Summary

- formation of ultrafine particles downstream DPFs or DOCs largely depends on dilution parameters (dilution ratio, dilution temperature...)
- ultrafine particles are formed downstream DPF or DOC due to condensation effects
- ultrafine particles formed downstream DOCs or DPFs obviously do NOT have a solid core

⇨ ultrafine particle formation is provoked by inadequate measuring conditions

BILD 11: Summary

Of course a number of question remained and new questions came up, Figure 12.

New Questionaire

Can we conclude from these results that ultrafine particles are NOT formed under real driving conditions?

What are "real" dilution conditions?
- "real" dilution ratios?
- "real" mixing conditions?

FIGURE 12: New Questionaire

These are very important questions which have to be answered very soon in order to give input necessary for the ongoing discussions.

And, finally, it is necessary to define a global standard for particle size distribution measurements. Otherwise - if different institutes measure under different conditions - results are hardly comparable and will lead to misinterpretations.

Conclusion

The results clearly emphasize the need to define a global standard for particle sizing!

FIGURE 13: Conclusion

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