Characterization of fine and ultrafine particles in emissions from CHP Plants in Denmark

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Introduction

CHP (Combined Heat and Power) plants are being increasingly used in Denmark due to their ability to utilize the heat generated from energy production. The type and magnitude of air emissions from CHP plants vary widely according to the energy source used and technology implemented for combustion and emission reduction. Ultrafine and fine particles emitted from nine Danish CHP Plants have been measured and characterized. The plants selected were fired by waste (WTE), biomass (BM), gas (GF) or gasoil (GO). A detailed description of the project is given in Fuglsang et al. (2009).

Methods

The methodology used for characterization of particles emitted from CHP plants were based on the following techniques:

- 1. Sampling of particles from the flue gas in a 12-stage low pressure cascade impactor (ELPI). Emissions of PM_{0.1}, PM₁ and PM_{2.5} were calculated from the real-time number concentrations measured by means of ELPI.
- 2. Analysis of the collected particles by:
 - SEM (Scanning Electron Microscopy): Analysis of morphology.
 - EDX (Energy dispersive X-ray spectroscopy): Analysis of elements in selected clusters of particles.
 - FIB-SEM (Focused Ion Beam-SEM): 3D cross section analysis of 2-3 selected particles.

Results and conclusions

The most abundant elements found by the EDX analysis in the different size fractions from the waste incineration plants and from the gas fired plants are shown in figure 1 and 2. The figures show representative results for these two plant types. For a description of the results from all plant types involved in the study, reference is given to Fuglsang et al. (2009).

In the figures below, the mass concentration in each size interval is indicated by marking the elements as follows: Bold: [10;100] % w/w; normal font: [2;10[% w/w; brackets: [0.2;2[% w/w.

Figure 1. Most abundant elements found by EDX analysis of the particles emitted from waste incineration plant WTE2. Particles sampled after the plant's ESP.



Figure 2. Most abundant elements found by EDX analysis of the particles emitted from the landfill gas fired CHP plant GF2.



FIB-SEM analysis of selected particles showed relatively large, hollow soot particles in the samples from gas fired engines. An example of a hollow soot particle is shown in figure 3. These hollow particles could be formed from rapid combustion of small droplets of lubrication oil entering the combustion chamber from the piston cylinder walls. Solid soot particles found by FIB-SEM from plant GF2 seemed to consist of a solid nucleus with a surface layer, probably formed by heterogeneous condensation of organic compounds during the combustion process.

Figure 3. Hollow, carbonaceous particle from gas fired plant GF1, cut through by means of FIB.



Key findings were:

- A significant enrichment of metals (e.g. Fe, Mn, Cu) in the PM0.1 and the PM1 fractions were found for particles from both WTE and BM plants.
- The particles from the WTE plants were generally found to be crystalline and porous in structure. A relatively high fraction of K and Na were found in the fraction between 0.1 μm and 1 μm. For PM > 1 μm, a high content of Ca, S, O and C were found. This is explained by the formation of CaSO4 during the desulphurization process at the WTE plants.
- Carbon and to some extend also oxygen dominates in the PM0.1 and PM1 fractions from the biomass, gas- and gasoil fired plants.
- Spherical soot particles dominate in the particles from the gas- and gasoil fired plants, and to a lesser extend also from the BM plants.
- The high number of particles emitted from the GF plants is most probably caused by the use of lubrication oil in the plants' gas engines.
- The FIB-SEM analysis of particles from the GF plants showed that spherical soot particles of a diameter of 150 nm 1500 nm from these plants may be hollow as well as solid.

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Characterization of fine and ultrafine particles from Combined Heat and Power (CHP) plants in Denmark



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Combined Heat and Power plants involved





Sampling setup





Sampling setup





Methods used for characterization





- SEM (Scanning Electron Microscopy)
- EDX (Energy Dispersive X-ray analysis)
- FIB-SEM (Focused Ion Beam-SEM)

Early microscope

FIB-SEM analysis





RESULTS for waste- and gas fired plants Morphology - size distributions - analysis of elements





Waste fired CHP plants: SEM analysis of representative particles





Waste fired CHP plants WTE2 (bag filter) Average size distribution



Waste fired CHP plants: Most abundant elements found by EDX - plant WTE2



Gas fired CHP plants: SEM analysis of representative particles





FIB-SEM 3D analysis: Plant GF2





FIB-SEM 3D analysis: Plant GF1





Gas fired CHP plants: Most abundant elements in particles from landfill gas fired plant GF2



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CONCLUSION (1)



WTE plants:

- The particles were generally crystalline and porous in structure.
- A significant enrichment of metals (e.g. Fe, Mn, Cu) were found in the PM0.1 and the PM1 fractions.
- A relatively high fraction of K and Na were found in the fraction between 0.1 μm and 1 $\mu m.$
- A high content of Ca, S, O and C in PM > 1 μ m may be explained by the formation of CaSO₄ and CaCO₃ during the desulphurization process.

CONCLUSION (2)



Gas fired plants:

- The high number of particles emitted is most probably caused by the addition of lubrication oil to the gas fired engines.
- Soot particles emitted may be hollow as well as solid.
- Soot particles consisting of a solid nucleus and a surface layer were probably formed by heterogeneous condensation during the combustion process.
- The formation mechanism for hollow particles could be related to rapid combustion of lubrication droplets in the engine.

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Report:

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