

## CHEMICAL AND STRUCTURAL ANALYSES OF AEROSOL AND FLY-ASH PARTICLES FROM FIXED-BED BIOMASS COMBUSTION PLANTS BY ELECTRON MICROSCOPY

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**ABSTRACT:** The interest in the mechanisms governing the formation of coarse fly-ash and aerosol particles in biomass combustion processes has constantly increased during the past few years. Besides ash and aerosol sampling with subsequent wet chemical analyses and theoretical mathematical modelling, electron microscopy has turned out to be a valuable and efficient method in this field of science. In this work, results from analyses by scanning electron microscopy and energy dispersive X-ray spectrometry performed on aerosol and fly-ash samples from the flue gas of biomass combustion units are presented. Comparing the results from the analyses of samples from test runs with different kinds of biomass fuels, it becomes obvious that the submicron and the coarse mode of the particulates show remarkable differences in shape and composition. While the submicron particles mainly consist of K, Na, S, Cl and heavy metals like Zn and Pb, the main compounds of the coarse mode are refractory species like Ca, Si, Mg and Al. Submicron particles are spheres or crystals while the coarse fly ash particles are amorphous (if molten) or consist of a grid built up by refractory species on which smaller particles agglomerated. This difference between the two modes is due to their different formation mechanisms. The analytical results correspond well with results achieved from experimental and theoretical work in the field of aerosol and fly-ash formation.

### 1. INTRODUCTION

During the past few years the formation and behaviour of coarse fly-ash and aerosol particles formed during biomass combustion processes have become a subject of major relevance for numerous research groups engaged in the optimisation of biomass combustion systems. Coarse fly-ash and aerosol particles affect both the operation and the emissions and therefore, the environmental compatibility of biomass combustion plants. Besides mathematical simulations of aerosol and fly-ash formation processes, particle sampling at pilot-scale and real-scale combustors with subsequent chemical and structural sample analysis is an important methodological approach in this field. While wet chemical analyses are applied to provide information about the chemical composition of particle collectives, electron microscopy has proven a suitable method for gaining information about the shape and composition of single aerosol and fly-ash particles. In this paper it is shown, how the application of electron microscopy to the analysis of aerosol and coarse fly-ash particles formed during biomass combustion processes can provide valuable information about the shape and chemical composition of particulates and also contribute to enhancing the knowledge about their formation and growth mechanisms.

### 2. PARTICLE SAMPLING

#### 2.1 Common methodologies

When investigating particulate emissions from biomass combustion plants usually total dust sampling equipment, low-pressure cascade impactors (LPI) and differential mobility analysers (DMA) are applied to determine the total dust load and the particle size distribution (PSD) of aerosol and coarse fly-ash particles in the flue gas. To gain infor-

mation about the chemical composition of the fly-ashes and aerosols, the samples taken with these devices can be additionally analysed by wet chemical measures. Wet chemical analyses of total dust samples provide information about the chemical composition of the whole particle collective emitted from a combustion process. By analysing samples from different stages of cascade impactors the relation between the chemical composition of the particles and the PSD can be determined. However, only particle collectives and not single particles can be investigated using these sampling devices.

#### 2.2 Single particle sampling

For an optimal application of electron microscopy, the sample taking methods should allow the identification of single particles on the sampling substrate. Therefore, particle agglomerations should be avoided in any case. Furthermore, the substrates should be tailored to electron microscopic examination. For these reasons the following particle sampling method was applied:

Isopore polycarbonate membranes with a pore diameter of 50 nm were fixed in a filter holder. The filter holder was inserted into the flue gas channel of a fixed-bed biomass combustion plant right behind the boiler at flue gas temperatures of approximately 200°C. The flue gas was sucked through the filter holder. Isokinetic sampling was applied to guarantee a representative sampling with respect to the different size fractions of the particles. This means that the flue gas velocity at the entrance of the filter holder was adjusted to the velocity of the flue gas in the duct by several nozzles mounted at the inlet of the filter holder. This method guarantees that the PSD of the coarse fly-ash and aerosols is the same in the sample flow and in the duct. To achieve a single layer of particles and avoid particle agglomeration by collision on the filter membrane surface, the sampling time, during which the flue gas is passed

through the filter, was kept very short (10 to 20 s).

Since the number concentration of coarse fly-ash particles in the flue gas is very low, compared to the amount of submicron aerosol particles, the amount of this particle fraction on the filter is also low. Therefore, in order to sample higher numbers of coarse fly-ash particles for subsequent analyses, a pre-cutter cyclone of a low-pressure impactor (cut diameter: 16  $\mu\text{m}$ ) was also used.

### 3. ANALYSES BY ELECTRON MICROSCOPY

#### 3.1 Sample preparation

To avoid interactions of the particles with ambient air and moisture, the samples were stored in a exsiccator during transport. A small part of the filter was cut off and fixed at a sample holder. To avoid specimen charging, the specimen were coated with a thin carbon layer (approximately 20-30nm). The coarse fly-ash particles taken from the pre-cutter cyclone were embedded in resin and subsequently polished.

#### 3.2 Analysis Equipment

The samples were analysed using a ZEISS Gemini 982 field emission scanning electron microscope equipped with a Noran Voyager X-ray analysis system (Si(Lie) detector, ultra-thin window).

#### 3.3 Shape analysis

The shape and the structure of single particles were determined from scanning electron microscopy (SEM) images. The aim was to determine the shape (spheres, crystals, sticks) and the aspect ratios of the particles and to find out whether they were agglomerates or not. With state-of-the-art SEM technology it is possible to identify even single particles with a diameter of 10 to 20 nanometers.

#### 3.4 Analysis of chemical composition of single particles

SEM-EDX (energy dispersive X-ray spectrometry) was used to determine the chemical composition of particles. Particles in a size range down to approximately 40 nm can be analysed by this method. It is also possible to achieve information about the distribution of elements over the particle surface by element maps.

Additionally, different primary electron energies can be applied when investigating larger particles. Higher electron energy means an increase in the penetration depth of the electrons and the composition of thicker layers can be elucidated (depth probing).

Since the polycarbonate membrane itself consists of carbon and oxygen, the signals detected are affected by the membrane itself for two reasons:

- Since the surface of the particles is not perfectly plane, the electron beam is scattered and signals from the membrane surface next to the particle are detected together with signals emitted from the particle itself. The effect decreases with increasing particle diameter.
- Especially when analysing very small particles, the penetration depth of the electron beam is greater than the particle diameter. Therefore, the C and O signals consist of contributions of both, the membrane and the particle. This effect also decreases with increasing particle diameter and decreasing penetration depth of the electron beam (lower primary electron energy).

Therefore, the influence of the membrane must be considered when evaluating the results for oxygen, in particular when investigating particles in the submicron range. Since the particles were additionally coated with carbon, the C signals cannot be used for evaluation.

#### 3.5 Analysis of particle collectives

X-ray mapping enables an automated qualitative analysis of a great number of single particles concerning the distribution of the elements. Due to the overlapping of some X-ray peaks (e.g.: S and Pb) and the low counting rate per pixel, the information gained from these analyses is qualitative rather than quantitative and therefore, only provides an overview over a larger area of the sample.

#### 3.6 Plausibility of the results

It must be taken into consideration that SEM-EDX analyses of polycarbonate filters allow only a small section of the filter to be examined. Due to the geometry of the filter holder separation effects can occur because of different flow conditions across the filter area. To check the plausibility of the results achieved, samples taken at the same sampling board with a low-pressure impactor were also analysed by wet chemical measures. According to the cut diameter of the different stages of the impactor, the chemical compositions of several size fractions between 0.0625 and 16  $\mu\text{m}$  were determined. Then the analytical results achieved with both methods for particles of the same size ranges were compared.

## 4. RESULTS AND DISCUSSION

In the following, results from analyses of aerosol and coarse fly-ash samples by SEM-EDX are presented. The samples were taken during test runs at two fixed-bed biomass combustion plants:

- plant 1: pilot-scale combustion plant (nominal boiler capacity: 440 kW<sub>th</sub>) equipped with a travelling grate.
- plant 2: moving grate combustion plant with a nominal boiler capacity of 3,000 kW<sub>th</sub>.

During the test runs chemically untreated wood chips, bark, fibre board and waste wood were used as fuels.

#### 4.1 Coarse fly-ash particles

Figure 1a shows submicron aerosol particles and a typical coarse fly-ash particle from beech combustion (plant 1). SEM-EDX analyses (Figure 1b) reveal that the aerosol particles (region 2 in Figure 1a) entirely consist of elements such as K, Na, Cl, S, Zn and Pb (the peaks of C and O originate from the filter material), which are volatile under typical fixed-bed conditions. This result indicates that these particles were formed by chemical reactions and subsequent condensation of gaseous ash-forming species present in the flue gas.

The analysis of the coarse fly-ash particle reveals that this particle mainly consists of refractory elements such as Ca and Mg (region 1 in Figure 1a). This fact proves that this particle is not an agglomerate of aerosol particles, but was formed at the grate and entrained with the flue gas.

With decreasing flue gas temperature volatile elements, which vaporised during the thermal decomposition of the fuel bed, form new particles by chemical reactions followed by nucleation and/or heterogeneous condensation on

the surface of the prevailing coarse fly-ash and previously condensed aerosol particles. This can be seen by analysing coarse fly-ash particles using different primary electron energies. The higher the electron energy, the greater the penetration depth of the electrons in the particle. Thus at high electron energies at least part of the X-ray signal is emitted from deeper layers of the particles (Figure 2).

Figure 2 shows the spectra of the same region, analysed at electron energies of both 7 and 15 keV. In case of homogeneous particles and due to the small differences in the X-ray energies of the Pb-M $\alpha$  / S-K $\alpha$  and K-K $\alpha$  / Ca-K $\alpha$  X-ray lines, their respective intensity ratios should be approximately independent of the electron energy. But Figure 2b shows a dramatic change in these ratios, which indicates a change of the particle composition, depending on the depth of the layer analysed. For instance, the high energy shoulder of the overlapping Pb and S peaks in the spectra, especially distinct in the 7 keV spectrum, results mainly from Pb. The change of the peak shape between the two spectra is a result of the changing Pb / S concentration ratio, indicating a higher Pb concentration on the particle surface than in the layer beneath. Comparing the C, K and Ca peaks, the C and K concentrations can also be assumed to be higher in the core than on the surface of the particle.

These results are clear for Ca (as a refractory element) and for C (amount of unburned char). The results for K show that K partly volatilises and partly seems to remain in the particle due to diffusional limitation.

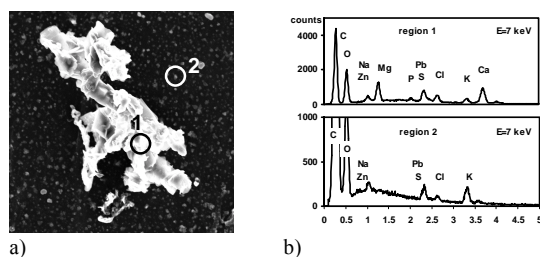


Figure 1: Aerosol particles and coarse fly-ash particle from beech combustion (plant1)

Explanations:

- a) SEM image, picture width: 16.4  $\mu$ m
- b) EDX spectra recorded at regions 1 and 2 of image a)

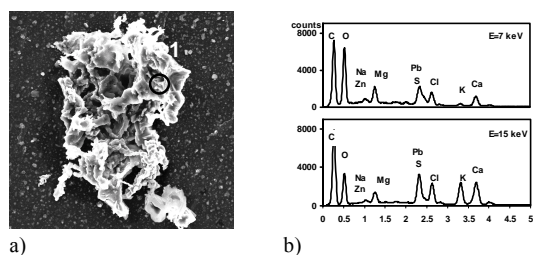
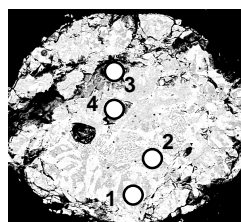


Figure 2: Aerosol particles and coarse fly-ash particle from beech combustion (plant1)

Explanations:

- a) SEM image, picture width: 22.9  $\mu$ m
- b) EDX spectra recorded with different electron energies of 7 and 15 keV from region 1 in image a).

Besides this commonest kind of coarse fly-ash particles, a second type was noticed in samples from bark combustion. This second type originates from mineral impurities enclosed in the fuel, which remain unburned and are entrained from the fuel bed with the flue gas. Figure 3 shows a SEM image of such a particle.



	O	Si	Mg	Al	Ca
	atom%				
1	58.8	13.1	7.0	0.5	19.2
2	60.0	12.3	3.2	8.1	15.1
3	60.6	13.2	4.2	4.3	15.1
4	53.5	16.4	4.4	7.5	15.9

Figure 3: Mineral fly-ash particle from bark combustion (plant 2)

Explanations: particle embedded in resin cross-sectioned and subsequently polished;  
SEM image picture width: 96  $\mu$ m,  
EDX analyses at primary electron energy of 7 keV at regions 1-4.

#### 4.2 Aerosols

Concerning the presence of elements forming aerosol particles, the results from the analyses of samples from test runs with bark (plant 2), waste wood and fibre board (plant 1) are comparable with those from beech combustion (see Figures 4, 5, 6). Again, the aerosols are formed by volatile elements which vaporise during thermal decomposition of the fuel bed. Obviously, the composition of the fuel strongly influences the composition and shape of the resulting aerosol particles.

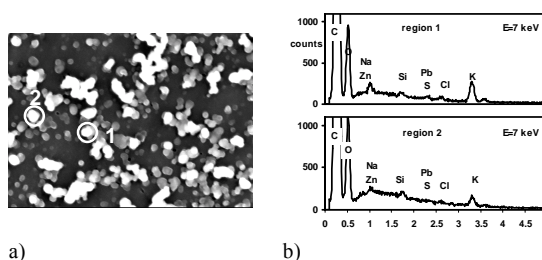


Figure 4: Aerosol particles from bark combustion (plant 2)

Explanations:

- a) SEM image, picture width: 3.8  $\mu$ m
- b) EDX spectra recorded at regions 1 and 2 of image a)

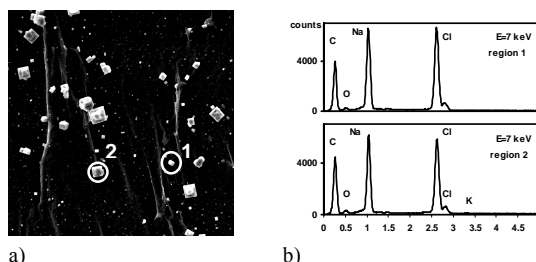


Figure 5: Aerosol particles from fibreboard combustion (plant1)

Explanations:

- a) SEM image, picture width: 38.2  $\mu$ m
- b) EDX spectra recorded at regions 1 and 2 of image a)

Due to the higher amounts of heavy metals like Zn and Pb, in bark, the aerosols formed during bark combustion also contain higher concentrations of these species. But, since the dominating elements are still K, Na, Cl and S, the shape of the particles keeps the same like for the results from beech combustion. Figure 4 also indicates that small amounts of refractory species (Si) can also serve as con-

densation nuclei for condensing species.

Caused by the high amount of Na and Cl in fibre boards, the aerosol particles shown in Figure 5 also contain high concentrations of NaCl. The particles have the typical cubic structure of salt crystals, and therefore their shape is completely different from the shape of aerosol particles from bark and beech combustion.

Another good example, illustrating the influence of the fuel composition on the shape and composition of aerosols, are the results gained from the combustion of waste wood, which is extremely rich in Zn and Pb. Figure 6 shows a SEM image and X-ray maps of aerosol particles sampled during waste wood combustion. Bar shaped particles consist mainly of Pb, Cl, K and S (presumably  $Pb_2KCl_5$ , or a mixture of  $PbCl_2$ ,  $KCl$ ,  $K_2SO_4$  and  $PbSO_4$ ), while spherically shaped particles contain high concentrations of Zn (presumably ZnO). These findings based on the X-ray mapping were also confirmed by SEM-EDX analyses of individual particles.

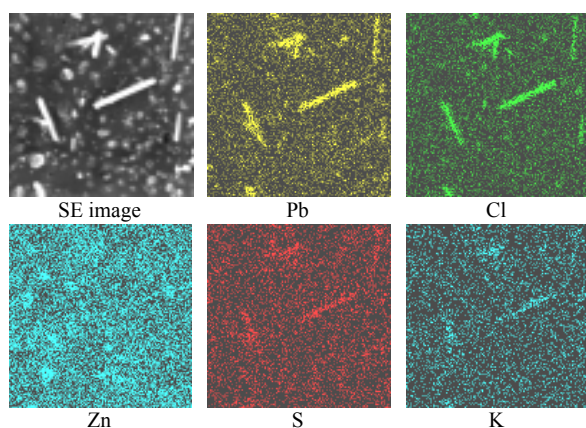


Figure 6: Secondary electron image and element distributions of aerosol particles from waste wood combustion (plant 1)

Explanations:

$E_0$ : 7 keV, picture width: 3.8  $\mu\text{m}$

## 5. CONCLUSIONS

From the SEM pictures and the results of SEM-EDX analyses shown in Figures 1 to 6, valuable information about the formation of coarse fly-ash and aerosol particles during the combustion of different biomass fuels can be derived.

Comparing the results from the analysis of samples from different test runs with several kinds of biomass fuels, it becomes obvious, that there exist remarkable differences in shape and composition between the submicron and the coarse mode of the particulates. While the submicron particles mainly consist of K, Na, S, Cl, and heavy metals like Zn and Pb, the main compounds of the coarse mode are refractory species like Ca, Si, Mg and Al. Submicron particles are spheres or crystals while the coarse fly ash particles are amorphous (if molten or mineral source) or consist of a grid built up by refractory species on which smaller particles agglomerated. This difference between the two modes is due to their different formation mechanisms. While submicron particles are formed by homogeneous nucleation or heterogeneous condensation of metal vapours

during the cooling phase of the flue gas, coarse fly ash particles consist of unburned char, mineral impurities or bottom ash already formed on the grate, which are entrained with the flue gas. Consequently, coarse fly-ash particles did not undergo phase conversion during their formation, which also explains their bigger size and different chemical composition.

The results presented in this paper correspond well with other theoretical and experimental work in the field of ash and aerosol formation during biomass combustion (1, 2). Therefore, SEM and SEM-EDX analyses obviously represent a proper and efficient method in this field, whether used as a stand-alone or as a supporting tool for the evaluation of wet chemical analyses of aerosol samples and for the evaluation and checking of aerosol and ash formation and behaviour modelling.

## 6. FUTURE DEVELOPMENTS

Future developments will focus on automated analyses of the geometric parameters and the chemical compositions of fly-ash and aerosol particles (3) as well as on the development of analytical standards (4).

Concerning automated SEM analyses limitations are set by specimen damage caused by the electrons and specimen drift. Presently, special methods and techniques are being developed and tested, which will help to solve these problems.

The accuracy of the quantitative results is often affected more strongly by specimen damage than by shortcomings of the quantification procedures with regard to particle size and shape. Special correction programs for particle analyses demand an analytical expression for the particle shape and may be of little use for particles of very irregular shape. Additionally, radiation damage can affect particles and bulk specimen in a different way. Therefore, it is necessary to develop a technique to produce standard particles, which resemble the unknown particles in both composition and structure, in order to be able to check the analytical results achieved and to detect and quantify possible analytical failures.

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