INVESTIGATION OF FORMATION PATHWAYS OF AEROSOL PARTICLES FORMED DURING FIXED BED COMBUSTION OF WOODY BIOMASS FUELS

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Introduction

The use of biomass combustion for the production of heat and electric power has already become an important factor for energy supply. A big share of this kind of energy supply is covered by fixed bed combustion of woody biomass fuels in combustion plants with a size range from a few kW of thermal output to large plants in the MW range. But all of these plants suffer more or less from ash related problems, which are deposition of fly ashes and subsequent slagging and fouling and additionally, particle emissions have to be prevented.

In order to decrease the ash related problems inside the combustion plants as well as harmful emissions, detailed knowledge about fly ash formation and deposition mechanisms is required. The results from these investigations are expected to be helpful for the implementation of measures, which can influence the formation and deposition of ashes.

Fly ash formation during combustion of woody biomass. In order to get more information about fly ash formation and behavior and to determine possible influencing parameters, investigations of fly ashes were performed by many researchers in the past for coal combustion as well as for biomass combustion (e.g. 1-4).

At the Institute for Resource Efficient and Sustainable Systems (RNS) investigations concerning biomass combustion were performed for three woody biomass fuels, which are frequently used in fixed bed furnaces for energy production, namely chemically untreated wood, bark and waste wood (5). The results have shown a bimodal particle size distribution (PSD). One mode, the coarse fly ash particles, consists of particles with a diameter larger than 1 µm, the particles of the second mode, the aerosols, are submicron. Chemical analyses of coarse fly ashes showed mainly compounds, which have under the given conditions in biomass furnaces a low volatility. The coarse fly ashes investigated consisted mainly of oxides and sulphates of Ca, Mg, Si and K.

The average chemical composition of aerosol particles could be obtained by wet chemical analyses of particles sampled on Berner-type low-pressure impactor (BLPI) stages. It could be derived that low volatile elements were enriched in coarse fly ash particles in opposite to volatile elements, which were enriched in aerosol particles. At least the distribution of Zn followed the PSD, which suggested an even distribution in the particles. These results could also be gained from scanning electron microscopy (SEM)/ electron diffraction X-ray spectrometry (EDX) analyses of single particles, which provided average compositions.

Regarding the aerosols, three particle formation theories could be derived (6). The different chemical compositions of biomass fuels lead to different release behaviours of aerosol forming elements and in the following to different particle formation pathways.

During the combustion of chemically untreated wood chips mainly ash forming compounds of the elements K, S, and Cl are released to the gas phase. These compounds may react further and undergo gas to particle conversion processes during flue gas cooling. The supersaturated ash vapours may nucleate or condense on the surface of particles, which are entrained directly from the fuel bed (primary particles). Due to chemical analyses of aerosol particles, which showed K, S and Cl as the main components, the presence of considerable amounts of primary particles, which could suppress nucleation of new particles, could be ruled out. Therefore, nucleation and afterwards condensation should be the dominating particle formation mechanisms.

Compared to pure wood fuels bark contains considerably more low volatile compounds of the elements Ca and Mg, but also more K, Cl, S and Zn. During the combustion process a certain amount of the low volatile compounds is directly released as primary particles in the submicron as well as in the supermicron size range. Especially the submicron primary particles, which contain mainly CaO according to chemical analyses, may provide surface for further condensation of ash forming vapours. Additionally, Zn plays an important role for aerosol formation during bark combustion. According to thermodynamic equilibrium calculations Zn is expected to evaporate during combustion on the grate and as soon as oxidising conditions prevail in the flue gas ZnO should form. ZnO has a very low vapour pressure and therefore it should immediately form particles, which subsequently act as seeds for further condensation of aerosol forming matter. Therefore, during the combustion of bark nucleation of new particles may be suppressed partially by primary particles (CaO) and ZnO particles.

A third main pathway for aerosol formation could be derived for the combustion of waste wood, which contains considerably higher amounts of Zn than pure wood and bark. This surplus of Zn compared to other fuels mainly originates from paintings. Due to the great amount of ZnO particles, which form in the way as described for bark combustion, a further nucleation of ash forming vapours may be suppressed completely.

The condensation of ash forming vapours on aerosols containing Ca and Zn has not been proved yet. For that reason the analyses of aerosol particles regarding their composition in the core as well as in the outer layer were aspired. The only way to achieve a sufficiently high resolution for such particle analyses was the use of transmission electron microscopy (TEM) in combination with EDX analyses. Therefore, aerosol samples were taken on copper grids from combustion plants and subsequently analysed by TEM.

Experimental

Aerosol sampling. The particle sampling was performed during the combustion of chemically untreated wood (spruce) and bark at the boiler outlet of a combustion plant with a 440 kW_{th} flame tube boiler. The samples were taken in the way that copper grids, which were precoated with a carbon layer, were fixed on polycarbonate filters. After that, flue gas from the boiler outlet was sucked over the polycarbonate filters for some seconds. Then the copper grids were removed from the filter and forwarded to the Research Institute for Electron Microscopy and Fine Structure Research in order to perform the TEM/EDX analyses.

TEM/EDX Analyses. For the visual characterisation of the aerosol particles, pictures were taken with a CCD camera and evaluated. Furthermore, in order to detect the compositions of the aerosol particles EDX spectra were taken. Firstly, to detect the composition of the particles' cores the analysis point was set in the centre of the particle image. Secondly, for the outer layer analysis the electron beam was placed in a way that it touched the particle shells.

The instrument used for these investigations was a Philips CM20/STEM with an acceleration voltage of 200 kV and a LaB_6 cathode. The EDX spectra were recorded using a light element detector (HPGe).

Results and Discussion

The particles found on the TEM-grids had various sizes between several nanometres and about 0.2 µm. It seemed that bigger particles,

which were found during previous fly ash characterisation investigations could not be caught with the copper grids. Nevertheless, the particles captured were in the right size range for TEM analyses (< 0.3µm). The visual evaluation of the particles showed mostly small agglomerate-like particles as it can be seen in Figure 1.

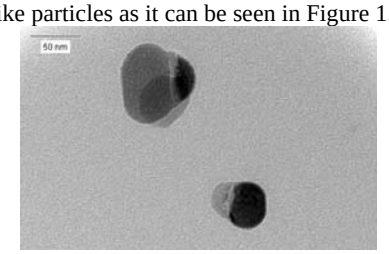

Figure 1. Picture of aerosol particles taken with a CCD camera

EDX analyses of aerosol particles from the combustion of wood chips (spruce) and bark showed that for chemically untreated wood the dominating species were K-compounds (mostly K_2SO_4) as it had been expected from former investigations. Also for aerosol particles from bark combustion K_2SO_4 and KCl were dominating the composition. Interestingly, no particles containing Ca could be found, which leads to the conclusion that Ca, although it had been detected in that particle size range by wet chemical analyses of impactor samples, originates from bigger particles, which could not be fixed on the TEM grids. The Ca in particles smaller than 200 nm in impactor samples was found most probably due to non-ideal particle precipitation efficiency of the impactor stages and particle bounce off to stages with smaller cut diameter.

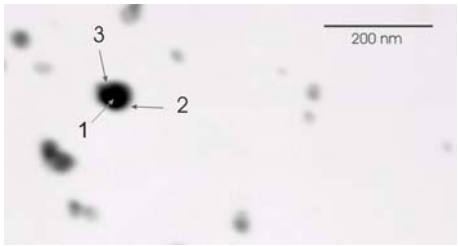

Figure 2. Locations of TEM analyses on aerosol particles

In order to determine if ZnO particles had been present before the formation of condensed K_2SO_4 and KCl, particles were investigated in more detail. During TEM analyses Zn was found in some aerosols from bark combustion. The particles were analysed at different points such as shown in Figure 2. The analyses of point 1 in Figure 2, which covered shell and core of the particle, showed a Zn/K mass ratio of 0.27 (± 20%). In contrast, the analysis of point 2, which just hit the particle shell, did not show any Zn. Point 3 showed a similar result as point 2. The analyses spectra of the points 1 and 2 are plotted in Figure 3. Generally, the Zn containing particles investigated showed this build-up. From that it could be concluded that Zn most probably had formed ZnO particles, which further acted as condensation seeds for other ash forming species. Regarding aerosol formation during waste wood combustion, chemical analyses of aerosol particles and simulation calculations suggest a higher suppression of nucleation of ash forming compounds by ZnO particles, but TEM/EDX analyses have still to be performed.

The formation pathways described could also be confirmed by aerosol formation simulations (7), which were performed in order to find the most influencing variables on formation mechanisms. Calculations of aerosol formation and behaviour in a biomass furnace with fixed grate and flame tube boiler were performed and the results were compared with measurements. In fact, modelling results similar to the measured results could be obtained when Ca and Zn were considered in the simulation as primary particles. Zn was inserted as peak of ZnO particles with a diameter < 0.1 µm and Ca was implemented as a broad peak of particles containing mainly CaO ranging from 0.3 to several hundred µm. Simulation results of PSDs and chemical compositions of the aerosols were similar to the measured values.

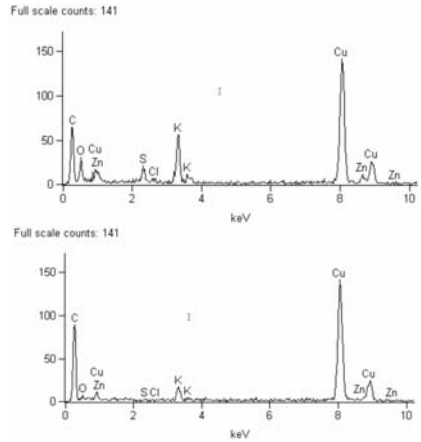

Figure 3. Spectra of point analyses no. 1 and 2 displayed in Figure 2

Conclusions

Investigations of aerosol formation during fixed bed combustion of chemically untreated wood, bark and waste wood were performed in order to derive influencing measures on particle formation and deposition. Three main aerosol formation pathways could be derived:

During the combustion of chemically untreated wood ash forming compounds of K, S and Cl are released into the gas phase and subsequently may react and further form particles by nucleation and condensation. During the combustion of bark submicron and supermicron Ca-containing particles are entrained from the fuel bed in considerable amounts. Especially the submicron particles provide condensation surface for further ash forming compounds and may suppress nucleation partly. For particle formation from bark combustion and especially from waste wood combustion Zn becomes important. As confirmed by thermodynamic data, the amounts of Zn released to the gas phase form mainly ZnO, which undergoes nucleation and condensation and forms particles with a diameter below 100 nm. These particles act as seeds for further condensation of alkali chlorides and sulphates as well as for gaseous heavy metal compounds and can therefore suppress nucleation to a certain extent depending on their concentration in the flue gas.

TEM analyses of aerosols in a size range below 200 nm from combustion of wood chips (spruce) and bark were performed in order to proof these theories. The results confirmed the expected particle formation pathways. Furthermore, these aerosol formation processes could be reproduced quite accurately by simulation calculations, which show results similar to measured PSDs and wet chemical analyses of aerosol particles.

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