AEROSOL AND FLY ASH FORMATION IN FIXED BED BIOMASS COMBUSTION SYSTEMS USING WOODY BIOFUELS

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ABSTRACT: At a pilot-scale and a large-scale grate-fired combustion unit test runs with different woody biofuels were performed with the aim to determine all relevant parameters for a detailed characterisation of aerosols and fly ashes. Therefore, particle size distributions and concentrations of fly ashes and aerosols in the flue gas downstream the boiler and upstream the dust separation device were measured, as well as samples for the subsequent determinations of the chemical composition and shape of particles by wet chemical and SEM-EDX-analyses were taken. Based on the results of these test runs and on aerosol formation and behaviour modelling, which was performed in parallel, formation mechanisms for aerosols and fly ashes, which are related to the chemical compositions of the fuels used were investigated. It is concluded, that, concerning combustion of woody biomass, three different formation processes, related to chemically untreated wood chips, bark and waste wood, can be suggested.
Keywords: aerosols, biomass, combustion, conversion, fixed-bed, fly ash

1 INTRODUCTION

Fixed bed combustion of woody biofuels such as wood chips, sawdust, bark and waste wood has already reached a considerably high level of technological development. However, certain problems related to aerosols and fly ashes formed during the combustion process are still unsolved.

In medium and large-scale combustion units deposits in the furnace and in the boiler/superheater can lead to severe operational problems resulting in unexpected plant shutdowns and reduced availability of the installations. With rising ash content of the fuel used these problems also increase.

Within the EU emission limits for particulate emissions are permanently decreasing, and specially for small and medium-scale biomass combustion units, highly advanced state-of-the-art dust separation systems (baghouse filters, ESP) are, due to their high costs, not applicable. Therefore, the development of highly efficient and economically affordable aerosol precipitation devices is urgently required.

To solve these problems, basic data about the main characteristics of fly ashes and aerosols (e.g. chemical composition, particle size distribution, concentration in the flue gas) formed during combustion as well as detailed information about the formation process itself are required. Former research regarding aerosol formation mainly focused on coal fired systems, on straw combustion and on fluidised bed combustion of biofuels. Regarding fixed-bed combustion of woody biofuels no reliable data were available and therefore, since this combination of combustion technology and fuels is of great relevance for most European regions, the ongoing EU Project BIO-AEROSOLS (ERK6-CT1999-00003), from which the results presented in this paper originate, was initiated.

2 THEORY

During fixed-bed combustion of solid fuels two fly ash fractions, the coarse fly ashes and the aerosols, are formed. These fractions significantly differ concerning their particle size and chemical composition as well as their formation mechanisms.

Coarse fly ashes are particles entrained from the fuel bed with the flue gas. They mainly consist of refractory species and their particle sizes can vary between some μm and some 100 μm.

In contrast with coarse fly ashes, the formation mechanism of aerosol particles is more sophisticated. During the combustion process a part of the volatile compounds, such as alkali metals, S, Cl and heavy metals is released from the fuel to the gas phase and subsequently undergoes homogeneous gas phase reactions [1, 2]. The saturation vapour pressure of the resulting compounds is in many cases far lower than that of the reactants, thus particle formation by nucleation or condensation of vapours on existing surfaces takes place. Subsequently, the particles formed grow by collision and coagulation processes. In fixed-bed combustion processes the final particle size distribution (PSD), resulting from particle formation by nucleation as well as particle growth by condensation and coagulation, is approximately a logarithmic normal distribution. The peak diameter of the PSD is always smaller than 1 μm.

The PSDs of coarse fly ashes and aerosols together form the typical bimodal PSD of particulate emissions from solid fuel combustion processes.

3 METHODOLOGY

To gain more detailed information about fly ash and aerosol formation during fixed-bed combustion of woody biofuels, two different approaches were chosen. Test runs at a pilot-scale and a large-scale biomass combustion unit were performed and mathematical modelling concerning the formation and growth of aerosols during combustion was carried out.

3.1 Test runs at combustion units

Several testing campaigns at a 440 kW_{th} pilot-scale and a 40.000 kW_{th} large-scale moving grate combustion plant were performed. While the large-scale plant is equipped with a water tube steam boiler, the pilot-scale

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unit is equipped with a fire-tube hot water boiler. Wood chips (spruce, beech), fibre-boards, bark and different types of waste wood were used as fuels.

Aerosol and fly ash measurements were performed in the flue gas duct downstream the heat exchangers and upstream the dust separation devices at flue gas temperatures of about 180 to 220°C. The following measurement and analyses techniques and methods were applied:
- Determination of the PSD and concentration of aerosols in the flue gas with 9-stage Berner-type low-pressure impactors (BLPI).
- Determination of the total fly ash load in the flue gas using the method according to VDI 2066.
- Sampling of aerosol and coarse fly ash particles on polycarbonate filter membranes for subsequent analyses by means of scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX).
- Sampling of aerosols and fly ashes with special hot gas filters directly in the combustion zone.
- Wet chemical analyses of particle samples taken with the BLPI. Analyses method: pressurised multi-step digestion of the ash samples ($HNO_3/HF/H_3BO_3$), element detection with ICP-MS or AAS.

Additionally, to characterise the fuel used, wet chemical analyses of the fuel were performed.

All chemical analyses of fuels, fly ashes and aerosols covered the elements Ca, Si, Mg, K, Na, S, Cl, Zn, Pb, Cd and Cu, which are supposed to be the most relevant components concerning aerosol and coarse fly ash formation during combustion of woody biomass [2, 3].

In Fig. 1 the experimental setup at the pilot-scale combustion unit is shown exemplarily.
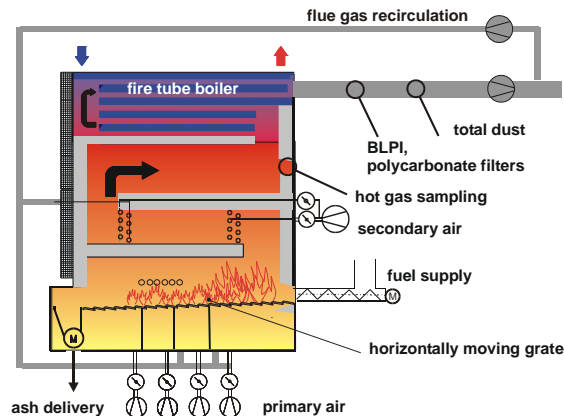

Figure 1: Experimental setup during the test runs at the pilot-scale combustion unit

3.2 Mathematical modelling of aerosol formation

The Plug Flow Aerosol Condenser (PFAC) is a mathematical model for simulation of the formation and evolution of a multi-component aerosol during cooling of a flue gas with a certain content of condensable vapours. The model was originally developed in the PhD-thesis of Christensen [2]. The model equations include homogeneous nucleation of pure substances, growth by multi-component gas-to-particle conversion and coagulation of spherical particles. The local gas phase composition is determined from a gas phase chemical equilibrium calculation combined with a finite reaction rate kinetics for slower reactions. In order to solve the model, the initial particle size distribution, the initial elemental molar fraction and the axial temperature profile have to be specified.

4 RESULTS

4.1 Characterisation of the fuel

In Table 1 results from wet chemical analyses as well as the moisture and ash contents of fuels used during the test runs at the pilot-scale and the large-scale combustion plant are shown.

Regarding elements relevant for formation of coarse fly ashes (Ca, Si and Mg), the lowest concentrations can be found in trunk wood (spruce and beech), while higher concentrations are found in bark and waste wood. Si is normally dominating in waste wood, Ca is the most relevant coarse fly ash forming element in bark.

Concerning aerosol forming species, the amounts of the total concentrations of K, Na, S, Cl and heavy metals rise from spruce over beech and bark to waste wood. From analyses results it can be derived, that specially for waste wood a wide range of concentrations of aerosol forming elements is possible.

Table 1: Results from chemical analyses of fuels fired
Explanations: d.b. … dry base; w.b. … wet base

Fuels fired at the pilot-scale combustion plant

		spruce	beech	bark	waste wood 1
moisture content	wt.% w.b.	53.3	9.7	49.2	33.9
ash content	wt.% d.b	0.3	0.6	5.6	5.0
Si	mg/kg d.b.	<400	165	2,251	9,039
Ca	mg/kg d.b.	789	1,412	12,122	9,863
Mg	mg/kg d.b.	124	294	820	1,417
K	mg/kg d.b.	513	1,045	2,878	1,192
Na	mg/kg d.b.	4.6	16.7	74.0	1,303.0
Cl	mg/kg d.b.	96.6	26.0	159.4	1,184.5
S	mg/kg d.b.	<150	112	364	1,132
Zn	mg/kg d.b.	9	5	80	687
Pb	mg/kg d.b.	0.4	0.5	3.1	547
Cu	mg/kg d.b.	0.9	1.1	5.3	19
Cd	mg/kg d.b.	0.08	0.05	0.43	0.77

Fuels fired at the large-scale combustion plant

		waste wood 2	waste wood 3	waste wood 4	waste wood 5
moisture content	wt.% w.b.	23.6	26.1	28.9	31.6
ash content	wt.% d.b	3.8	4.4	4.5	7.8
Si	mg/kg d.b.	4,470	8,841	10,171	14,478
Ca	mg/kg d.b.	3,887	5,551	3,520	6,664
Mg	mg/kg d.b.	389	467	637	793
K	mg/kg d.b.	736	615	598	784
Na	mg/kg d.b.	849	868	846	957
Cl	mg/kg d.b.	3,974	944	366	520
S	mg/kg d.b.	995	849	635	1,314
Zn	mg/kg d.b.	10,817	562	704	687
Pb	mg/kg d.b.	563.8	197.4	71.1	721.6
Cu	mg/kg d.b.	233.8	10.9	34.3	22.9
Cd	mg/kg d.b.	12.83	2.04	0.63	0.97

4.2 Results from total fly ash measurements

In Fig. 2 mean values as well as maximum and minimum values of the total fly ash emissions measured during test runs at the pilot-scale combustion unit are plotted against the ash contents of the fuels used (see also Table 1). These results clearly indicate, that with increasing ash content of the fuel also the fly ash emissions rise.

It can also be seen that the fly ash emissions measured during the combustion of one specific kind of fuel considerably scatter. This is mainly due to variations of the plant load. With increasing load of the combustion unit also the combustion air and flue gas velocities increase and consequently, more ash particles are entrained from the fuel bed. During the test runs the load of the pilot-scale unit was varied between 30 and 100% of its nominal boiler capacity.

Another known influencing parameter on fly ash formation, which is not investigated within this project, is the combustion technology (fixed-bed, fluidised-bed, circulating fluidised-bed).
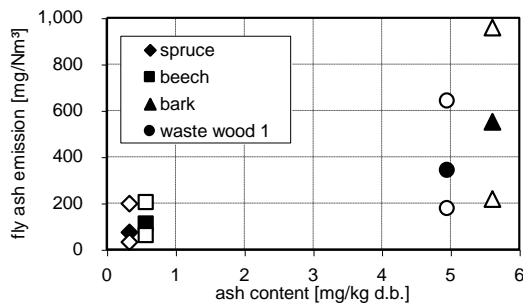

Figure 2: Ash content of the fuel vs. fly ash emissions
Explanations: data normalised to dry flue gas and 13 vol.% O_2; full marks: mean value; empty marks: minimum and maximum values

4.3 PSD and concentration of aerosols in the flue gas

In Fig. 3 results from determinations of the PSD with the BLPI are shown. The data represent mean values based on a minimum of 3 measurements per fuel. It can be seen, that the PSD has always one distinct peak. From the comparison of the PSDs with the results from the fuel analyses (Table 1) it can be derived, that the higher the content of K, Na, Zn and Pb in a fuel is, the more aerosols are formed. The detailed evaluation of the test runs also indicate, that all other parameters investigated (excess air ratio, furnace temperature, fuel moisture content, flue gas recirculation) have no significant influence on the mass and PSD of the aerosols formed.

From Fig. 3 and Fig. 4, in which the mass mean diameter of the PSDs determined with the BLPI is plotted against the concentration of particles <1μm, it can be seen, that with increasing aerosol load also the peak diameter of the PSD increases. The detailed analyses of the data indicate, that the total number of particles formed is always in the same range (about 10^7 to 10^8 particles/cm³). Results from the pilot-scale and the large-scale plant are presented in Fig. 4 and obviously, there is a slight influence of the combustion unit on the final particle size of the aerosols. The effect, that the particles formed in the large-scale unit are somewhat bigger, is supposed to be due to the different time-temperature profiles of the two furnaces and boilers.
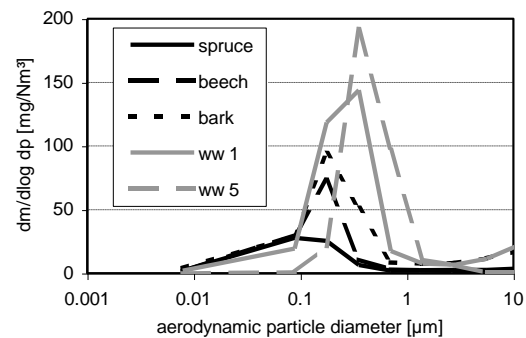

Figure 3: Particle size distribution of aerosols
Explanations: data normalised to dry flue gas and 13 vol.% O_2; ww … waste wood
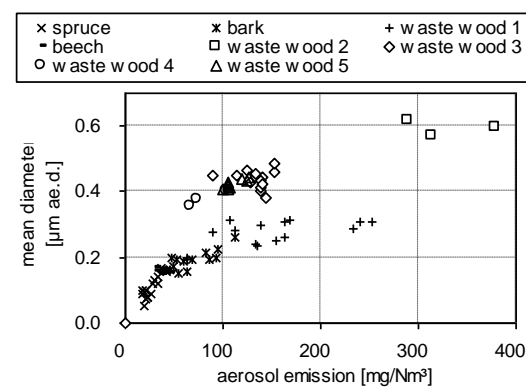

Figure 4: Aerosol emission vs. mass mean diameter
Explanations: data normalised to dry flue gas and 13 vol.% O_2

4.4 Chemical composition of aerosols

In Fig. 5 the average compositions of the aerosol fractions formed during the test runs with different fuels determined by wet chemical analyses of BLPI-foils is given. Based on these data and the chemical composition of the fuels, the following statements concerning similarities and differences of aerosols formed during the combustion of different types of woody biomass fuels can be derived:

In terms of mass of aerosols formed, Na, K, Zn, and Pb are the most relevant elements. Depending on the S and Cl contents of the fuels, these metals are bound as chlorides, sulphates and oxides as well as in case of metal excess as carbonates.

Concerning the concentrations of the aerosol forming elements mentioned in the fuel, in trunk wood (wood chips from spruce and beech), only K is of relevance. Consequently, the aerosols formed mainly consist of K-salts. Comparing the fuel analyses with the analyses results for aerosols it can also be seen, that the Cl/S-ratio in beech is about the same like in the aerosols formed during beech combustion.

Bark contains significantly higher concentrations of all relevant aerosol forming elements (especially K and Zn) than trunk wood. Consequently, also higher concentrations of Zn can be found in the aerosols formed. In contrast to all other fuels tested, also considerable Ca-concentrations occur in aerosols from bark combustion. Ca cannot be vaporised under the temperature conditions prevailing in fixed-bed biomass combustion units, and therefore, the basic aerosol forming mechanisms of

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nucleation and condensation, mentioned in section 2, are not valid for Ca. As SEM-analyses of bark have shown [5], very small CaO particles (in a size range down to some μm) are embedded in the structure of the bark. It can be assumed, that as a results of the rapid heating in the furnace, these particles are fragmented to a particle size smaller than 1 μm, and subsequently are entrained from the fuel bed with the flue gas. SEM-EDX analyses of aerosols sampled with polycarbonate filters at the boiler outlet during bark combustion have confirmed the presence of CaO particles in the submicron mode [6].
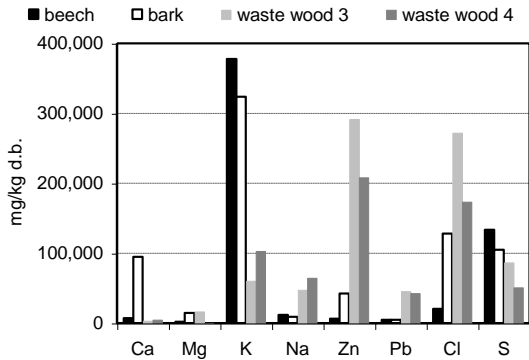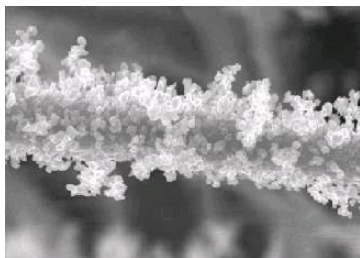

Figure 4: Chemical composition of aerosols

	atom%
Si	27.2
Ca	0.2
Mg	0.0
Na	1.0
K	1.2
Zn	5.6
Pb	0.0
S	0.9
Cl	0.0

Figure 5: SEM-image and results from EDX-analyses of aerosols sampled in the hot furnace during waste wood combustion
Explanations: Si-values originate from the filter material; picture width: 6.66 μm

The K-concentrations in waste wood are in the same range as those in trunk wood and therefore, lower than those in bark. But, in contrast with the other fuel types, the Na, Zn, and Pb-concentrations are significantly higher. Consequently, the contribution of the heavy metals and Na to the aerosol formation increases and K becomes less important. Specially the high Zn-concentrations cause a significant change in the aerosol formation mechanisms compared to the other fuels investigated. Concerning trunk wood combustion it can be assumed, that during the cooling phase of the flue gas, K-salts become supersaturated and form particles by homogeneous nucleation. During bark combustion additionally CaO-particles act as nucleation nuclei. For waste wood combustion it must be considered, that, in a reducing atmosphere (on the grate) elemental Zn can vaporise [4]. As soon as oxygen is available, Zn is oxidised to ZnO(s) and particles in the range of about 10 nm are formed. This is supposed to happen in an early stage of the process, and due to the high Zn-concentrations in waste wood, further nucleation of aerosol forming species is suppressed by condensation on the surfaces of the ZnO nuclei. The presence of ZnO

nuclei is confirmed by SEM-EDX analyses presented in Fig. 5. The samples were taken with a specially constructed probe directly in the hot furnace before the boiler inlet (see Fig. 1, hot gas sampling port) at about 1,000°C.

4.5 Results from modelling

Besides the test runs, modelling of aerosol formation and behaviour was performed to evaluate the effect of operational parameters and fuel chemistry on the physics and the chemical composition of the aerosols generated. A parametric study considering the following conditions was conducted:
- increased entrainment of ash, to gain information about the influence of coarse fly ashes on aerosol formation,
- the effect of fuel chemistry.

Concerning the influence of the amount of the coarse fly ash particles (entrained ash) on aerosol formation, the following results were achieved:
- With increasing particle entrainment from the fuel bed the mass of aerosols formed slightly decreases. The results have shown, that an increase of entrained ash by approximately 1,500% would be needed to reduce aerosol formation by 10% by enforcing condensation on the surfaces of the entrained ash.
- Furthermore, the results from modelling indicate, that in case of an increased condensation of aerosol forming species on the surfaces of entrained ashes, sulphates tend to condense on the surfaces while chlorides remain in the aerosol fraction.

Moreover, the effect of fuel chemistry and particularly the Cl:2S-ratio in the fuel was investigated. From Fig. 6, it can be seen that the aerosol mass loading increases when the major form of potassium is shifted from sulphate (at Cl:2S = 10%:90%) to chloride (at Cl:2S = 90%:10%). In the sulphate dominated system app. 140 mg aerosols/Nm^3 are generated, while in the chloride dominated system app. 345 mg aerosols/Nm^3 are formed.
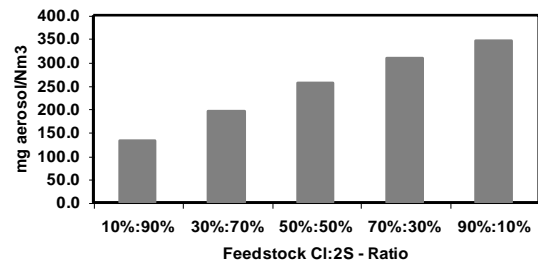

Figure 6: Aerosol mass density, mg aerosols/Nm^3, predicted as a function of the Cl:2S-ratio
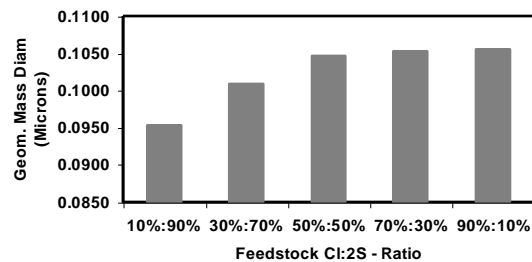

Figure 7: Aerosol mass geometric mean, μm, predicted as a function of the Cl:2S-ratio

The same picture is seen for the geometric mass mean diameter, which is increasing with rising Cl-content up to about 50% Cl and 50% 2S, above which the geometric mass mean diameter remains almost constant in the range of 0.105 μm (see Fig. 7).

Besides the performance of parametric studies, the PFAC was also applied to predict aerosol formation for the constraints (chemical composition, temperature, operation mode of the furnace) that were given during the test runs. Concerning the combustion of spruce, PFAC predicted an aerosol mass loading (mg aerosols/Nm³ flue gas) almost twice as high as measured during the test runs. This is supposed to be due to the fact that full release (100%) of K, S and Cl from the fuel to the gaseous phase was assumed, which may not necessarily be the case. For the beech fuel, the release of K, S and Cl was estimated based on a mass balance performed at the pilot-scale combustion unit. In this case, the PFAC-simulations predicted aerosol emissions in the range of 60 to 70 mg/Nm³ which are about 10% higher than the results gained from the test runs. Taking into consideration, that particle losses caused by heterogeneous condensation on the tube surfaces were neglected, these modelling and experimental results are in good compliance.

Due to a lack of data concerning the CaO and ZnO nuclei formation mentioned in section 4.4, the model can at the moment not be applied for the simulation of aerosol formation in bark and waste wood combustion processes.

5 CONCLUSIONS

From the results of the test runs as well as of the modelling the following conclusions concerning fly ash and aerosol formation during fixed-bed combustion of woody biomass can be drawn.

Coarse fly ash emissions of a biomass furnace mainly depend on the ash content of the fuel and the load of the combustion unit. With an increase of these parameters the probability of particle entrainment from the fuel bed with the flue gas also increases.

The mass of aerosols formed during combustion mainly depends on the chemical composition of the fuel used. The higher the concentrations of K, Na, Zn and Pb are, the higher the aerosol emissions will be. Modelling as well as the results of the test runs have revealed, that besides the fuel composition, no other parameters (furnace temperature, load, etc.) significantly influence the mass of aerosols formed. Furthermore, the chemical composition of the aerosols also almost exclusively depends on the chemical composition of the fuel fired. Concerning the particle size distribution of aerosols determined during test runs at two different combustion units it can be concluded, that the time-temperature-profile of the combustion unit may have a slight influence on the peak diameter of the resulting particle size distribution.

Theoretical considerations and results from modelling, as well as the results gained from test runs at the pilot-scale and the large-scale combustion unit lead to the suggestion that during combustion of woody biomass three different aerosol formation processes depending on the type of fuel used take place.

The first process prevails when firing chemically untreated wood chips, where aerosol formation and growth are mainly due to nucleation and condensation of K-salts (chlorides and sulphates) followed by coagulation processes.

During the combustion of waste wood the behaviour of Zn becomes more important. Under reducing conditions elemental Zn can be released from the fuel into the gas phase. When oxidation takes place, ZnO(s) nuclei are formed. This is supposed to happen right after the flue gas leaves the fuel bed. In the following, further nucleation of alkali-metal and heavy metal-salts is suppressed by condensation on the large surface provided by the high number of ZnO-nuclei and particles grow due to condensation and coagulation.

Bark behaves somewhere in between the two mechanisms already explained. Submicron CaO-particles entrained from the fuel bed and ZnO(s) particles formed according to the mechanism mentioned, do in most cases not provide the surface area needed to suppress nucleation, so that K-salts still form new particles. Subsequently the CaO, ZnO and K-salt particles grow by further condensation of metal salts on their surfaces and by coagulation.

Following these mechanisms, it can be concluded, that, during waste wood combustion, a considerable part of the aerosols is formed in the furnace, while for bark and specially for trunk wood combustion, aerosol formation mainly takes place in the boiler.

6 REFERENCES

[1] FRIEDLANDER S.K., 1977: Smoke Dust and Haze, John Whiley and Sons, New York, USA

[2] CHRISTENSEN K. A., 1995: The Formation of Submicron Particles from the Combustion of Straw, Ph.D. Thesis, ISBN 87-90142-04-7, Department of Chemical Engineering (ed), Technical University of Denmark, Lyngby, Denmark

[3] OBERNBERGER I., DAHL J., BRUNNER T., 1999: Formation, Composition and Particle Size Distribution of Fly Ashes from Biomass Combustion Plants. In: Proceedings of the 4th Biomass Conference of the Americas, Sept 1999, Oakland (California), USA, ISBN 0 08 043019 8, Elsevier Science Ltd. (Ed.), Oxford, UK, pp. 1377-1385

[4] OBERNBERGER I., 1998: Fractionated heavy metal separation in Austrian biomass-fired grate combustion plants – approach, experiences, results. In: Ashes and particulate emissions from biomass combustion, Series Thermal Biomass Utilization, Vol. 3, BIOS (ed.), Graz, Austria, dbv-Verlag, ISBN 3-7041-0254-7

[5] ZEVENHOVEN-ONDERWATER M., 2001: Ash-forming matter in biomass fuels, Ph.D. Thesis, ISBN 952-12-0813-9, Grafia OY, Abo, Finland

[6] OBERNBERGER I., BRUNNER T., JOELLER M., 2001: Characterisation and formation of aerosols and fly ashes from fixed-bed biomass combustion. In: Proceedings of the IEA-Seminar "Aerosols from Biomass Combustion", June 2001; Zurich; IEA Bioenergy Agreement, Task 32 "Biomass Combustion and Co-Firing" (ed.), TNO, Apeldoorn, NL, ISBN 3-908705-00-2, pp 69-74