

Modeling of aerosol formation during biomass combustion for various furnace and boiler types

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Abstract

In the frame of the EU-financed project BIOASH an existing model for simulating aerosol formation during combustion was improved and adapted for biomass combustion systems in order to contribute to a better understanding of aerosol formation and behavior and to the solution of ash-related problems in biomass furnaces and boilers. Subsequently, the model was applied for several test cases (test runs performed within the BIOASH project) in order to compare and evaluate modeling and measurement results.

The model is a plug flow model considering gas phase modeling by means of thermodynamic equilibrium calculations and a kinetic approach for modeling gaseous sulfate formation. The main particle formation mechanisms nucleation, condensation and agglomeration as well as particle precipitation mechanisms (diffusion, thermophoresis, turbophoresis, inertial impaction and gravitational settling) as well as the condensation of ash forming vapors on boiler walls are considered.

Results of modeling aerosol formation in different kinds of combustion units were compared with results from measurements regarding PSD and chemical composition of the aerosol particles at boiler outlet. The modeling results show a good match with the experimental results, which indicates the good applicability of the model. Moreover, the different properties of the aerosol particles regarding PSD and chemical composition due to different combustion and boiler technologies and different biomass fuels, which result in different formation pathways, become obvious.

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1. Introduction

The thermal use of biomass instead of fossil fuels and nuclear power for the production of heat and electric power is an important contribution to a sustainable energy supply. A great variation of biomass fuels from wood pellets to straw co-fired with coal is used in combustion units with a thermal power ranging from a few kW to several hundred MW. But state-of-the-art biomass combustion plants are still affected by several kinds of problems, which lower their availability and economic efficiency. Among them so-called ash-related problems, which are on the one hand deposit formation inside of furnaces and

boilers with subsequent slagging, fouling and corrosion and on the other hand particulate emissions, play an important role. Especially inorganic combustion aerosols are of interest since they contribute strongly to both groups of ash-related problems, deposit formation as well as particulate emissions with their subsequent environmental impact.

In order to solve ash-related problems in biomass combustion units much R&D work has already been performed. Nevertheless, many questions are still unsolved and need further investigations. Therefore, modeling of ash formation, precipitation and deposit formation during biomass combustion is performed in order to achieve a better understanding of the most relevant mechanisms for these processes and to enable the development of technologies to influence these processes in a way that the corrosion and fouling potential as well as the emission of fine particles from biomass combustion units can be reduced.

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First attempts of modeling the formation and behavior of inorganic combustion aerosols were made concerning coal and waste combustion often considering the fate of heavy metal emissions [16,12,22,7,24]. Simulations of aerosol formation during biomass combustion were performed by [5] and [6] calculating the aerosol formation during the combustion of straw. Furthermore, several researchers investigated particle formation and particle deposition behavior also by means of Computational Fluid Dynamics (CFD) simulations, which allows a more detailed approach of modeling the particle formation and deposition processes during combustion [36,21,17,27,25].

But the simulation models mentioned focused mostly on coal combustion and if biomass combustion was considered, mostly the combustion of straw was the topic. Furthermore, if particle formation mechanisms were treated in detail, either alkali metal compounds or heavy metal compounds were considered for particle formation from the gas phase. Additionally, CFD based models, which were also developed mostly for coal combustion, concentrated on deposit formation and the relevant particle deposition mechanisms. Therefore, in order to evaluate aerosol formation and behavior during the combustion of woody biomass fuels with a detailed view at particle composition and particle size distribution (PSD) at the boiler outlet a new model was set up. The model includes the relevant particle formation mechanisms for aerosol particles as well as all relevant chemical compounds for the formation of aerosols during the combustion of woody biomass fuels in grate furnaces including waste wood as well.

Aerosol formation during the combustion process takes place because some elements form volatile compounds, such as alkali metals (K, Na), S, Cl and heavy metals (Zn, Pb) and are released from the fuel bed to the gas phase. Subsequently, these compounds may react and further become supersaturated due to a lowered vapor pressure of the new compound formed or simply due to the cooling of the flue gas. The supersaturation of the respective compounds results in a phase change, which may be nucleation of new particles or condensation on existing particle surfaces. Once particles have formed, they collide with each other and may adhere or coalesce, which leads to a decrease of particles in the flue gas but an increase of the particle diameters.

The mechanisms of aerosol formation have been investigated for combustion of woody biomass [2,26] as well as for combustion of coal [28,4]. During combustion of woody biomass different aerosol formation pathways can happen depending on the fuel composition. The investigations of the aerosols formed have shown that during the combustion of chemically untreated wood compounds of the elements K, S and Cl dominate the aerosol fraction. During bark combustion Zn, Na and Ca additionally become relevant and for waste wood Zn and Na compounds may play a dominating role for aerosol formation. Due to the higher temperatures during combustion of coal as well as during biomass co-firing in coal power plants also refractory compounds including the elements Ca, Mg and Si may undergo nucleation and condensation processes, which lead to an enrichment of these compounds in the aerosol

fraction. Additionally, the fragmentation of the ash contributes stronger to aerosol formation than during combustion of woody biomass.

2. Model description

2.1. General model description

The aerosol formation model was set up as a one dimensional plug flow model. Therefore, no backward effects and recirculation zones could be considered.

Moreover, the gas phase modeling is done by means of thermodynamic equilibrium calculations and by the implementation of a kinetic approach to model gas phase sulfur reactions. In order to consider aerosol formation and precipitation the mechanisms nucleation, condensation and agglomeration as well as the particle deposition mechanisms (thermophoresis, particle diffusion, turbophoresis, inertial impaction and gravitational settling) as well as vapor condensation on furnace and boiler surfaces were implemented.

Furthermore, the aerosol formation model was restricted to the formation of particles of inorganic compounds that are stable under oxidizing flue gas conditions. Thus, aerosol formation is not modeled in the primary combustion zone, where reducing conditions may prevail locally, but starts with the secondary air injection. Therefore, initial conditions for the simulation, which are represented by the initial flue gas properties such as temperature, pressure, gas composition and the size distribution of primary particles (particles entrained from the fuel bed by the flue gas), were determined for this point. Especially the possibility of inserting primary particles in various sizes, amounts and various chemical compositions allows considering the constraints for modeling aerosol formation during combustion of different biomass fuels.

In addition to the initial conditions, boundary conditions had to be defined, which are flue gas and wall temperature, gas pressure, gas velocity and the gas residence time in the respective calculation volume.

The data for the set up of initial and boundary conditions for the calculations as well as data for the comparison of measured and calculated aerosol properties were gained from test runs performed with selected biomass fuels and from element mass balances based on these test runs. In order to divide the ash forming elements released from the fuel into a gaseous and a solid fraction (primary particles), thermodynamic equilibrium calculations were performed in order to determine the compounds, which are under conditions prevailing in the primary combustion zone most probably solid or liquid. In addition to these compounds, certain amounts of volatile compounds, which form vapors according to the thermodynamic equilibrium calculations, were added to the primary particle composition due to the fact that a certain part of volatiles is embedded in the residual ash matrix. The amounts of these unreleased volatile compounds were considered by release factors gained from the mass balances mentioned [8]. The PSDs of these primary particles were determined from the PSDs of single ash fractions such as furnace fly ash, boiler fly

ash and coarse fly ash at boiler outlet, which were weighed according to their mass flow and subsequently superimposed.

The calculation results cover the total mass load of aerosol particles in the flue gas, the aerosol PSD, the chemical composition of the aerosol particles as well as the flue gas composition at different positions of the plant. A more detailed description of the aerosol formation model was given by [15].

2.2. Gas phase composition

The determination of the local gas phase composition is important for the prediction of mass, chemical composition and size distribution of aerosol particles, since most of the aerosols form by gas to particle conversion. Thus, the composition of the gas phase is determined at the beginning of each calculation step by performing a thermodynamic equilibrium calculation. For this calculation only gas phase compounds are considered in order to achieve possible supersaturations, which are needed to subsequently calculate gas to particle conversion processes. In order to guarantee the applicability of the thermodynamic gas phase calculation model, the most stable compounds of the following elements were evaluated by test calculations for woody biomass fuels: Al, C, Ca, Cl, Fe, H, K, Mg, Mn, N, Na, O, P, Pb, S, Si, Ti and Zn.

But the applicability of thermodynamic equilibrium calculations is restricted since the formation of gaseous sulfur compounds is known to be kinetically limited at flue gas temperatures below approximately 820 °C [23]. This kinetic limitation was implemented in the model by an Arrhenius-approach according to [6]. In this approach the oxidation reaction of SO₂ to SO₃, which is supposed to be a precursor of sulfates, is considered as the limiting step for gaseous sulfate formation.

Moreover, heterogeneous reactions between gas phase and fly ash particles happen. From these reactions especially the sulfation of CaO in ash particles is relevant. Since for modeling of this process detailed structural and chemical information about the ash particles is required, which is not available so far, sulfation reactions are considered prior to the aerosol formation simulation with a conversion factor of maximum 20% of the Ca in the particles formed.

2.3. Particle formation mechanisms

The particle formation mechanisms considered in the model are homogeneous nucleation of new particles and heterogeneous condensation of ash vapors on existing particles as well as particle coagulation.

For the process of homogeneous nucleation the modeling approach developed by [11] was used for the calculation of the nucleation rate in this aerosol formation model. Nucleation starts with the random formation of small molecule clusters, which can either grow or evaporate until they have reached a critical radius. Exceeding the critical radius they become stable and will only grow further. The critical radius of the nuclei is very sensitive to the surface tension of the condensable compounds, which is therefore a very important input parameter for modeling. The surface tension itself is dependent on the

particle radius as expressed by the so-called Tolman relation (using the parameter Tolman length). This relation describes the deviation of the surface tension from the macroscopic surface tension for very small droplets (particle diameter $\ll 1 \mu\text{m}$). But since data for the Tolman length could not be found in literature for the relevant ash forming compounds (see below) this effect had to be disregarded and the temperature dependent macroscopic surface tension was used for the calculations.

Heterogeneous condensation is considered by implementation of a relation derived by [10]. This relation expresses the molecular rate of condensation on particles for the entire range of the particle size.

The condensable species considered in the calculations for gas to particle conversion are K₂SO₄, KCl, (KCl)₂, K₂CO₃, Na₂SO₄, NaCl, (NaCl)₂, ZnO, ZnCl₂, PbO and PbCl₂ for all fuels investigated as well as CaO for coal combustion as well as biomass co-firing in coal combustion plants.

While gas to particle conversion processes change the total amount of solid and liquid phases, this mass remains constant during the process of coagulation, which affects only the PSD. Due to the different motions of the aerosol particles relative to each other, which can be caused either by Brownian motion [9] or by external forces such as gravity (according to [13]) or turbulent eddies in the flue gas [31], collisions between the particles occur. For each mechanism collision frequency functions, which represent coagulation probabilities are calculated separately. Moreover, in the model described coagulation is treated as coalescence and the particles are always treated as absolute spheres.

2.4. Particle and vapor deposition mechanisms

The main mechanisms in combustion devices which cause particle deposition are gravitational settling, inertial impaction, turbophoresis, thermophoresis and particle diffusion.

For the calculation of the amount of settled particles in combustion systems with continuously moving flue gas the approach of stirred settling was used because it describes settling in a permanently mixed gas [13]. Using this approach and the so-called terminal settling velocity, which has to be determined for each particle size, the amount of particles precipitated due to gravity was calculated.

The process of inertial impaction for coarse particles is considered by the approach of [14] and [37]. They derived a relation for the impaction efficiency of particles in a flow around a cylinder such as a boiler tube as function of the particle Stokes number. The relation can be applied to the whole particle size range because it is valid also for particles, of which the movement cannot be described with the Stokes law. Inertial impaction on boiler tubes is relevant only for coarse particles, since aerosols will follow the gas flow. Additionally, during tube flow particle inertia will lead to precipitation of aerosols due to turbophoresis, which characterizes that particles caught by turbulent eddies of the gas stream are thrown towards the wall and subsequently precipitated.

Particles exposed to a temperature gradient in the surrounding gas move into the direction of decreasing temperature,

which is called thermophoresis. For the calculation of the thermophoretic velocity several different relations have been published. In the model described a relation for the thermophoretic velocity and the thermophoretic coefficient by [33] was used because it is valid for the whole particle size range observed. In the case of simulating aerosol formation in a fire tube boiler a relation derived especially for particle deposition during tube flow was used for the calculations [30].

Furthermore, in a particle-laden gas stream a gradient concerning particle concentrations will always form in boundary layers, because unlike gas molecules submicron particles do not rebound from the walls. Therefore, a particle diffusion flux towards the wall is established. For the special case of deposition during turbulent tube flow, which is the case in flame tube boilers, a common approach used for particle removal by diffusion and turbulent eddies is used in the model developed [20].

In addition to particle formation and deposition processes, direct condensation of aerosol forming species on furnace and boiler walls occurs. This mechanism is considered using the approach for condensation of vapor mixtures in the presence of inert gases according to [35].

Particle and vapor deposition processes always occur together with erosion, shedding and re-entrainment of particles, which play an important role for the deposit formation process. In the plug flow model these processes must be considered by a general re-entrainment factor between 0 and 1 for each particle size section. Generally, submicron particles are not assumed to rebound from the wall and re-entrainment of submicron particles occurs mainly due to shedding which leads to a re-entrainment factor near to 0. On the other hand, coarse fly ash particles are assumed to rebound on average several times before deposition. Therefore, the re-entrainment factor for coarse fly ash particles is near to 1.

2.5. Mathematical description and numerical solution

A general mathematical description of aerosol formation and transport processes of particles of different size classes in a control volume has been given by the General Dynamic Equation (GDE) (Eq. (1)).

$$\begin{aligned} \frac{\partial \varphi}{\partial t} + (\nabla \cdot \varphi v_{\text{gas}}) + \sum_{k=1}^n \frac{\partial}{\partial m_k} (\varphi \cdot I_k) = \dots \dots \\ = \nabla \cdot D_p \cdot \rho_{\text{gas}} \cdot \nabla \cdot \left(\frac{\varphi}{\rho_p} \right) \\ + (\nabla \cdot \varphi v_p) + s_{\text{hom}} + s_{\text{coag}} \end{aligned} \quad (1)$$

In this equation the change of the particle size distribution function φ with time t in a control volume is determined by the source and sink terms for particle coagulation s_{coag} , particle growth, homogeneous nucleation s_{hom} , vapor condensation as well as particle diffusion into and out of the control volume, particle motion due to the gas velocity v_{gas} and due to the relative velocity v_p of the particles. v_p is caused by external forces such as gravity and thermophoresis and, together with

particle diffusion, may lead to particle deposition. Condensation is considered as condensation mass flux I_k of all n compounds ($k=1..n$) and diffusion is determined with the diffusion coefficient D_p and gas as well as particle density ρ_{gas} and ρ_p .

The particle size distribution (PSD) is represented by the so-called nodal point method [16], which treats the PSD as a discrete size distribution, whereas the sections are reduced to their mean diameters. The number of size sections has to be adapted to the modeling problem in order to achieve results of sufficient accuracy. In this study the number of sections was set to 125 with diameters equally logarithmically distributed between 10^{-3} and $1.6 \cdot 10^3 \mu\text{m}$.

Additionally, besides the aerosol population balance, a balance of the gas phase components was implemented. The set of equations to be solved covers therefore balancing equations for all particle classes, and for the condensable and non-condensable compounds respectively. The system is solved by spatial discretisation in the flow direction, whereas during one calculation step the operation conditions were assumed to be quasi-stationary. During each calculation step in the modeled control volume, firstly the gas composition was determined by a thermodynamic equilibrium calculation. Then particle formation and deposition processes were calculated in random sequence in order to average the influence of calculation order. As final step for each calculation sequence the balances were updated.

The whole model was developed as Visual Basic for Applications (VBA) Code using MS Excel® for data input and output. For the integration of the thermodynamic equilibrium calculations into the whole calculation procedure the commercial software Chemsheet® was used, whereas the thermodynamic data were exported from FactSage®.

3. Experimental

In order to characterize the aerosols formed during combustion of various fuels in different combustion units measurement campaigns were performed at a pilot-scale combustion unit with a flame tube boiler (nominal boiler capacity 440 kW_{th}) operated with wood chips from spruce, at a waste wood fired CHP plant (nominal boiler capacity 40 MW_{th}) and at a large-scale pulverized fuel fired power plant using a mixture of coal and sawdust (amount of sawdust 12 weight% wet base, which corresponds to 4% on energy base; nominal electric capacity 220 MW_{el}, mean calculated boiler load during the measurement campaign 404 MW_{th} ≈ 80% of nominal boiler load).

For the evaluation of the particle properties aerosols were investigated at boiler outlet. The particle size distributions and total mass loads of aerosols were determined with a conventional 9-stage Berner-type low pressure impactor (BLPI). The chemical compositions of aerosol samples from selected impactor stages were subsequently analyzed by means of wet chemical analyses. The measurement points for the BLPI measurements were in the flue gas duct behind boiler outlet for the pilot-scale combustion plant (mean flue gas temperature 189 °C), in the flue gas duct behind the economiser for the CHP plant (mean flue gas temperature 178 °C) and in the flue gas duct before air preheater for the power plant (mean flue gas temperature approx. 345 °C).

Beside impactor measurements at boiler outlet impactor measurements in the furnace section [3] as well as samples of fuel, bottom ash, furnace fly ash, cyclone fly ash (pilot and CHP plant) and total suspended particles at boiler outlet were taken and subsequently analyzed. Additionally, measurements of the flue gas composition at boiler outlet including HCl and SO_x were performed. Together with the operation data from the combustion plants investigated mass balances were set up, which enabled to create input data for the aerosol modeling calculations.

4. Measurement and calculation results

4.1. Measurements

Due to the different chemical composition of the fuels used during the three test runs, different aerosol formation pathways as well as different aerosol mass loads and chemical compositions were expected. The mean chemical compositions of the fuels are shown in Table 1.

The fuel analysis results show that chemically untreated wood chips (spruce) used in the pilot-scale combustion plant have the lowest ash content as well as the lowest concentrations of all ash forming elements from the three fuels investigated. Waste wood from the CHP plant, which corresponds to the qualities A1 to A4 according to German quality standards [29], has the highest ash content of the three fuels as well as the highest concentrations of Ca, Mn, Na, Pb, Si and Zn. Finally, the analysis of the mixture of coal and sawdust shows the highest element concentrations for Al, Cl, Fe, K, Mg, P and S. The concentration of Ti could not be compared, since it was only determined for the mixture of coal and sawdust.

The comparison of wood chips and waste wood indicates, that during combustion of waste wood a clearly higher amount of aerosols should be formed according to the higher concentrations of the aerosol forming elements Cl, K, Na, Pb, S and Zn in the waste wood. Additionally, while the composition of aerosols formed during combustion of wood chips should be dominated by K compounds (K_2SO_4 , KCl,

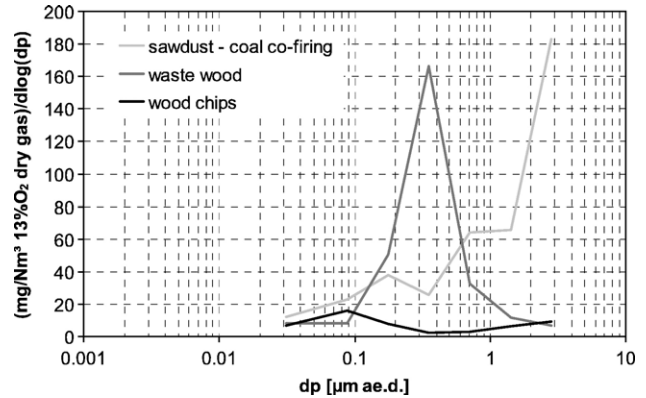


Fig. 1. Mean measured particle size distributions of aerosols at boiler outlet during combustion of wood chips (spruce), waste wood and sawdust co-fired with coal.

K_2CO_3), aerosols from waste wood combustion should not only contain K, S and Cl but also relevant amounts of Na, Pb and Zn. Furthermore, according to [26] the main formation pathways of aerosols from the combustion of wood chips should be the nucleation of alkali sulfates and subsequent condensation of other compounds on these particles. During combustion of waste wood, firstly ZnO particles should form, which cause further condensation of ash forming compounds on their surfaces suppressing the nucleation of alkali compounds.

Moreover, the formation of aerosols from the combustion of coal is expected to be strongly influenced by refractory compounds as described in section 1. The composition of the ash forming elements in the mixture of coal and sawdust is dominated by Al and Si and shows in addition high concentrations of Ca, Cl, Fe, K, Mg, Na, S and Ti. Opposite to biomass fuels in coal large amounts of the aerosol forming elements are bound in mineral phases [32,34] and not organically associated. Therefore, a different release behavior of the aerosol forming elements to the gas phase than for biomass fuels is expected.

The mean measured particle size distributions of aerosols at boiler outlet during the three measurement campaigns are shown in Fig. 1. The particle size distributions shown are based on 7 precipitation stages, of which the first is the final filter and the other stages are the impactor stages 1 to 6 with cut diameters of 0.0625, 0.125, 0.25, 0.5, 1 and 2 μm aerodynamic diameter (ae.d.). The values in Fig. 1 are related to the logarithmic mean particle diameters of the respective impactor stages, which correspond to 0.088, 0.177, 0.354, 0.707, 1.414 and 2.828 μm . As aerosols all particles smaller than 1 μm (ae.d.) are considered.

Aerosols from combustion of wood chips in the pilot-scale combustion unit, which have a mean mass load of 14.1 mg/Nm^3 (related to 13 vol.% O_2 and dry gas), have their peak on the first impactor stage with a cut diameter of 0.0625 μm (ae.d.). The average amount of aerosols in the flue gas formed during combustion of waste wood in the CHP plant is 84.2 mg/Nm^3 (related to 13 vol.% O_2 and dry gas) and the peak is located at the third impactor stage (cut diameter 0.25 μm ae.d.). Opposite to the pure biomass fuels the mean particle size distribution of

Table 1
Mean fuel compositions of wood chips (spruce), waste wood and a mixture of coal and sawdust sampled during the measurement campaigns performed

Parameter	Wood chips		Waste wood		Coal–sawdust mixture	
	Mean	st.d.	Mean	st.d.	Mean	st.d.
m.c.	25.7		27.2		9.5	2.1
Ash	0.8		16.4		13.7	2.0
H	6.3		4.4		4.4	
C	49.0		39.1		71.1	
N	0.1		0.9		1.4	
Al	155		5263	1028	16,731	3266
Ca	1705	380	8289	8646	4635	332
Cl	51.1	9.5	1195	145	1945	573
Fe	135	56.0	6123	162	6872	1470
K	446	39.8	2453	495	2991	743
Mg	178	28.7	1337	352	2737	249
Mn	99.0	3.4	262	44.5	101	13.9
Na	58.3	20.1	2707	22.1	1527	190
P	31.1	3.5	354	223	360	52.9
Pb	0.8	0.2	141	275	34.1	18.0
S	75.8	4.3	1503	32.4	7338	882
Si	905	403	46,657	663	23,746	5030
Ti	n.d.	n.d.	n.d.	n.d.	741	162
Zn	10.9	3.9	794	321	33.1	8.8

Explanations: amount of sawdust in mixture — 12 wt.% wet base.; elemental analyses in mg/kg dry base; ash — ash content in wt.% dry base; m.c. — moisture content of the fuel in wt.% wet base; analysis methods: [1], production of coal ash was performed according to coal standard at 815 °C; n.d. — not determined; st.d. — standard deviation; wood chips (spruce) — mean of 5 samples, waste wood — mean of 3 samples, coal-sawdust mixture — mean of 3 samples.

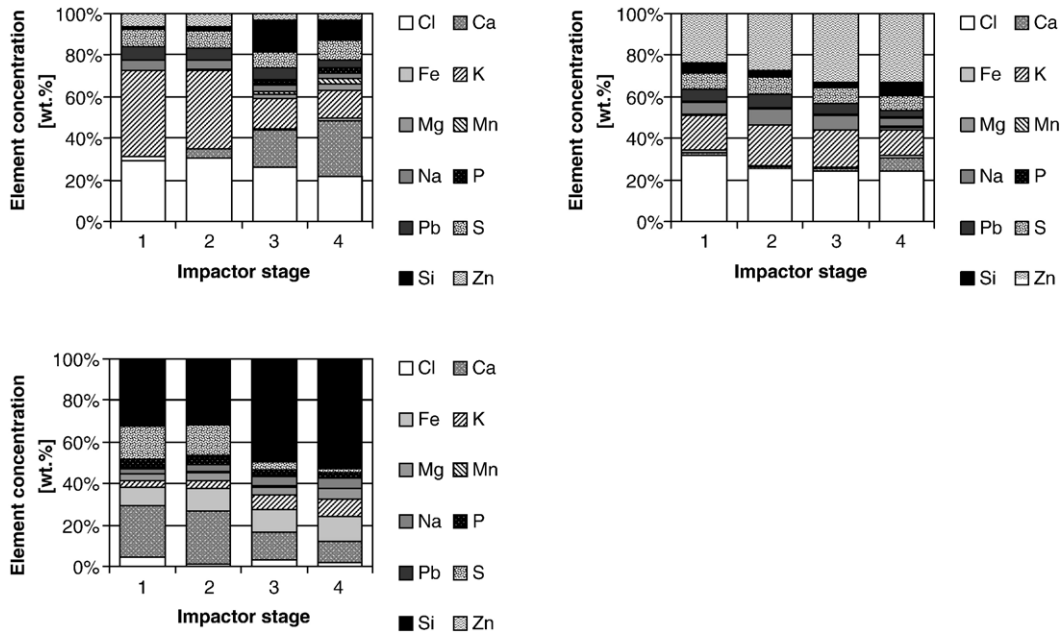


Fig. 2. Aerosol particle compositions at boiler outlet during combustion of wood chips (spruce), waste wood and sawdust co-fired with coal.

aerosols resulting from co-combustion of coal and sawdust (mean mass load 55.1 mg/Nm³ 13 vol.% O₂ dry gas) shows two modes in the size range below 1 μm (ae.d.), namely at the second impactor stage (cut diameter 0.125 μm ae.d.) and on the fourth impactor stage (cut diameter 0.5 μm ae.d.), which results in a trimodal PSD of co-combustion fly ash. Since other researchers did not observe the second peak during their measurements [18] the origin of the peak is not clear and an effect of the measurement equipment on the PSD cannot be ruled out.

A comparison of the chemical composition of aerosol particles sampled during the three measurement campaigns is shown in Fig. 2. The analyses were performed by means of wet chemical analysis [2]. It has to be mentioned that the concentration of Al in the particles could not be analyzed accurately, since the sampling foils were made of Al.

The aerosol particle analyses show that the chemical composition of aerosols formed during combustion of chemically untreated wood chips (spruce) is dominated by Ca, Cl, and K. Na, S, Si and Zn are also present, but in minor amounts. The concentrations of Cl, K, Na and Zn in the particles decrease with increasing particle diameter whereas the concentrations of Ca and Si increase with increasing diameter. For S no clear trend could be observed. This different behavior can clearly be related to aerosol formation from the gas phase and therefore an enrichment in the smaller aerosol fractions (Cl, K, Na, Zn) and entrainment of coarse fly ash particles from the fuel bed (Ca, Si). The other elements shown for aerosols from the combustion of chemically untreated wood chips (spruce) in Fig. 2 are present in traces (Fe, Mg, Mn, P, Pb).

Furthermore, for aerosol particles formed during combustion of waste wood analyses show that the major elements are Cl, K and Pb. Additionally, Ca, Na, S, Si and Zn are present in minor amounts as well as Fe, Mn and P are present in traces. In the

submicron particle size range investigated the concentrations of Ca and Zn increase with increasing particle diameter. The concentrations of the other major and minor elements have no clear trend related to the particle size.

Finally, the major elements in aerosols formed during co-combustion of coal and sawdust are Ca, Fe, S and Si. Cl, K, Mg, Na and P are present in minor amounts and Mn, Pb and Zn are present in traces. The concentrations of Ca, P and S decrease with increasing particle diameter, the concentrations of Fe, K, and Si increase with increasing particle diameter and for the concentration of Cl Mg and Na no clear trend could be observed.

4.2. Calculations

From the evaluation of combustion plant operating data as well as from the element balances performed on base of the measurement campaigns initial and boundary conditions for the

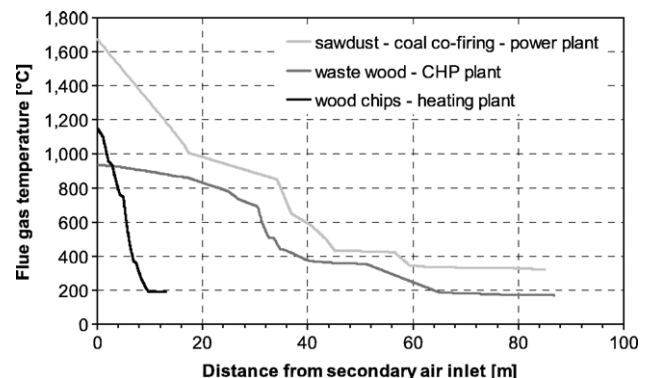


Fig. 3. Temperature profiles of the mean flue gas temperatures along the flue gas pathway for three different biomass (co-)combustion plants investigated.

aerosol formation simulations were performed as described in Section 2.

In Fig. 3 the temperature profiles for the three different combustion units from the secondary air inlet to the impactor measurement port at boiler outlet are plotted. For the starting temperatures at the secondary air inlet the calculated adiabatic flame temperatures were used. Moreover, it can be seen that in the pilot-scale heating plant the calculated flue gas path until boiler outlet is with 13 m much shorter than in the CHP plant (~87 m) and in the power plant (~85 m). Due to the fact that the impactor measurement port in the pilot-scale plant and the CHP plant has been before the cyclone the measured flue gas temperatures at the measurement ports are similar (<200 °C). However, the measurement port in the power plant has been before air preheater and thus the flue gas temperature at this point has been considerably higher (~350 °C).

As a result of the different flue gas path lengths the cumulated mean residence times of the flue gas in the furnace and boiler sections differ strongly for the different plants. The results are shown in Fig. 4. While in the pilot-scale combustion plant the cumulated residence time is below 2 s, it amounts to approximately 10 s in the CHP plant and more than 18 s in the power plant. For the residence time calculation in the CHP plant and in the power plant the acceleration of the flue gas due to cross section constrictions by tube bundles were not considered. The cumulated residence time in these two plants is therefore a little overestimated. Moreover, from Figs. 3 and 4 it becomes obvious that the time for aerosol formation is much longer in the CHP and in the power plant than in the pilot-scale heating plant, which implies stronger temperature gradients in the flue gas. Therefore higher supersaturations of ash forming elements in the flue gas are expected, which favors nucleation of new particles instead of condensation of ash vapors on existing particles.

Further important input data are the amounts of ash forming elements in the flue gas as well as the composition and size distribution of particles released from the fuel to the gas phase. The total amount of gaseous ash forming matter and ash particles, which are entrained with the flue gas was derived from the element balances performed. These balances also allowed the determination of release factors for single ash forming

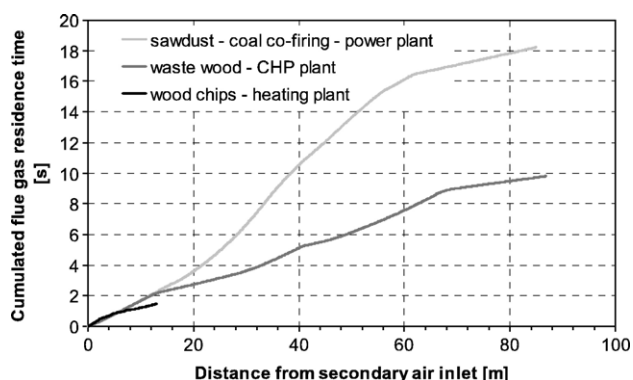


Fig. 4. Profiles of cumulated flue gas residence time along the flue gas pathway for three different biomass (co-)combustion plants investigated.

Table 2

Element release factors for simulation of aerosol formation during (co-) combustion of wood chips (spruce), waste wood and sawdust co-fired with coal

Element	Wood chips	Waste wood	Coal-sawdust mixture
Ca	0%	0%	1.5%
Cl	100%	100% ^a	100%
K	16%	5%	6%
Na	24%	2%	23%
Pb	100% ^a	43%	100%
S	72%	35%	98%
Zn	90% ^a	38%	87%

^aAssumptions used due to non-plausible release factors achieved from test runs.

elements, which represent the ratio of the element mass flow released to the flue gas to the total element mass flow introduced with the fuel. Ash particles entrained from the fuel bed are not considered as released. Therefore, the split of the ash forming matter into particulate matter entrained with the flue gas and gaseous ash forming matter is performed according to the release values gained. In Table 2 release factors for the relevant ash forming elements (Ca, Cl, K, Na, Pb, S, Zn) are given. If reasonable release factors could not be obtained from the element balances, for example when the mass balance could not be closed with sufficient accuracy, assumptions for the release factors had to be made. All other ash forming elements were assumed to be to 100% in the solid phase.

Additionally, using the element mass flow data derived as input, thermodynamic equilibrium calculations were performed in order to estimate the chemical composition of the particles, which were released from the fuel to the gas phase. The resulting mean particle compositions for the three fuels investigated are shown in Table 3. From the data in Table 3 it can be seen that the composition of particles entrained from the fuel bed during combustion of wood chips (spruce) is dominated by CaO, MgO and SiO₂. The particle composition of released particles from waste wood combustion has much

Table 3

Mean calculated compositions of particles released from the fuel during combustion of wood chips (spruce), waste wood and sawdust co-fired with coal

Compound	Wood chips	Waste wood	Coal-sawdust mixture
Al ₂ O ₃	2.86%	7.65%	19.39%
Ca ₃ (PO ₄) ₂	0.71%	0.16%	0.50%
CaO	48.32%	8.76%	8.09%
CaSO ₄	0.00%	2.19%	0.00%
Fe ₂ O ₃	0.00%	4.52%	4.74%
K ₂ SO ₄	1.35%	0.00%	0.00%
KAlSi ₃ O ₈	0.00%	0.40%	5.16%
MgO	14.87%	3.26%	9.23%
Mn ₂ O ₃	0.32%	0.31%	0.07%
Na ₂ SO ₄	0.40%	0.00%	0.00%
NaAlSi ₃ O ₈	0.00%	0.52%	4.14%
SiO ₂	31.07%	70.78%	47.41%
TiO ₂	0.00%	1.13%	1.22%
ZnO	0.10%	0.32%	0.04%

Explanations: particle compositions determined with thermodynamic equilibrium calculations; temperature range considered — 800–1200 °C; input data for the calculations were amounts of elements leaving fuel bed according to mass balances performed; the maximum amounts of elements in solid compounds were calculated according to the release factors determined.

lower contents of Ca and Mg compounds, but considerably higher amounts of Al, Fe, Si and Ti compounds, which can be related to the different fuel compositions (Table 1). The composition of fly ash particles formed during the co-combustion of coal and sawdust is, according to the fuel composition, dominated by Al, Ca, Fe, K, Mg, Na, Si and Ti compounds.

The amounts and PSDs of these particles were derived from particle size analyses of fly ash samples gained from the measurement campaigns. In Fig. 5 the PSDs for particles entrained from the fuel bed during combustion of wood chips (spruce), waste wood and co-combustion of coal and sawdust are outlined. The highest amount of entrained particles formed during co-combustion of coal and sawdust due to the relatively high ash content of the fuel and the PF-firing technology, where approximately 80% of the ash follow the flue gas through the boiler. The big difference of the two grate-fired fuels results from the big difference regarding their ash contents.

Subsequently, based on the input data shown above, aerosol formation calculations were performed. The results gained are mass load, PSD and chemical composition of aerosols at boiler outlet of the respective combustion units.

In order to compare the calculated and measured PSDs, the calculated PSDs had to be transformed to a PSD, which simulates the measurement with an impactor. This transformation was performed by calculating the precipitated amount of particles of a modeled size class with the impactor stage precipitation efficiency according to [19].

Fig. 6 shows calculated and measured PSD of aerosols at boiler outlet during combustion of wood chips (spruce). The PSD shows the same tendency as the measured PSD with the peak on the first impactor stage (cut diameter 0.0625 $\mu\text{m ae.d.}$) but the total mass load is with 9.3 mg/Nm^3 smaller than the measured one (14.1 mg/Nm^3 , both values related to 13 vol.% O_2 and dry gas). The difference originates probably from the fact that the single sub-models described in section 2 are approximations and thus the particle precipitation mechanisms may be overestimated as well as the plug flow model approach generally is a simplification. The larger deviation of calculated and modeled PSD are caused by the PSD of entrained particles,

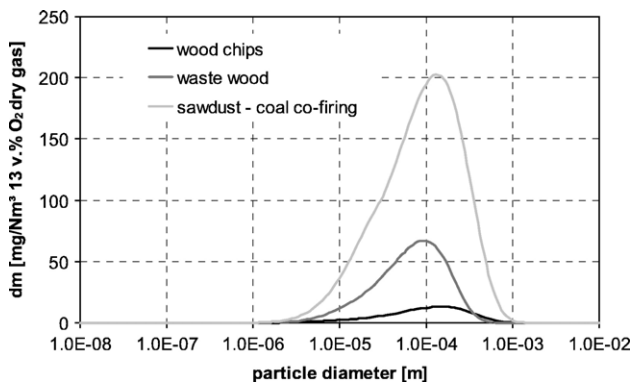


Fig. 5. Approximated mass size distributions of particles released from the fuels during combustion of wood chips (spruce), waste wood and sawdust co-fired with coal.

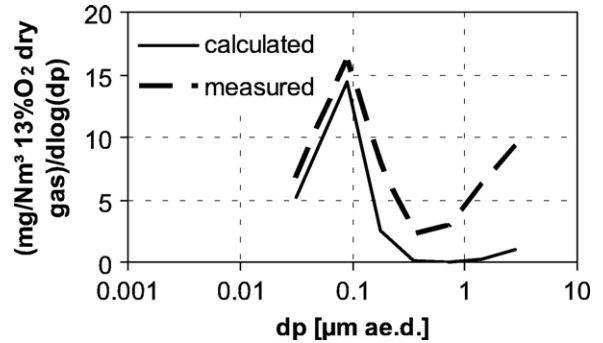


Fig. 6. Measured and calculated particle size distribution of aerosols formed during the combustion of wood chips (spruce) in a pilot-scale heating plant at boiler outlet.

which is an input parameter for the calculations and which may have a big effect on calculated PSD and chemical composition of aerosol particles. Additionally, possible deviations of the mean fuel composition used for modeling from the mean fuel composition during the impactor measurements have to be taken into account.

A comparison of the measured (Fig. 2) and calculated composition (Fig. 7) of aerosols formed indicates that the major aerosol forming elements were Cl, Ca and K for both cases. Moreover, Na, S, Si and Zn could be confirmed as minor aerosol forming elements by the simulations. The main element concentration trends related to the particle diameter, which were observed from the measurement results, could be reproduced. But the calculated concentrations of Ca, Mg, P and Si in aerosols differ a little from the measured concentrations which can be related to the PSD of primary particles in the submicron size range, which has to be set as input parameter.

The formation pathway, which is mainly the nucleation of K compounds (K_2SO_4 , KCl) and subsequent condensation of ash forming vapors on these particles could be confirmed by the simulation.

Furthermore, the simulation of aerosol formation during combustion of waste wood in a CHP plant results in a similar PSD as obtained from the measurements. The peak is also located on the third impactor stage with a cut diameter of 0.25 μm (Fig. 8). The calculated total mass of aerosols amounts to 87.2 mg/Nm^3 , which is a little larger than the measured mass of aerosols of 84.2 mg/Nm^3 (both values related to 13 vol.% O_2 and dry gas).

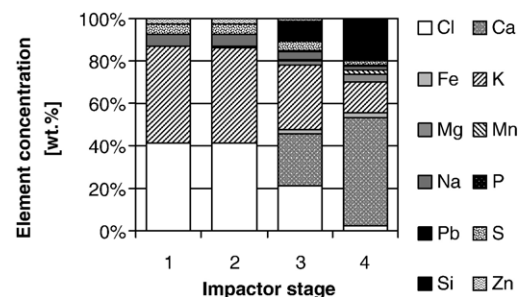


Fig. 7. Calculated particle composition of aerosols formed during combustion of wood chips (spruce) in a pilot-scale heating plant at boiler outlet.

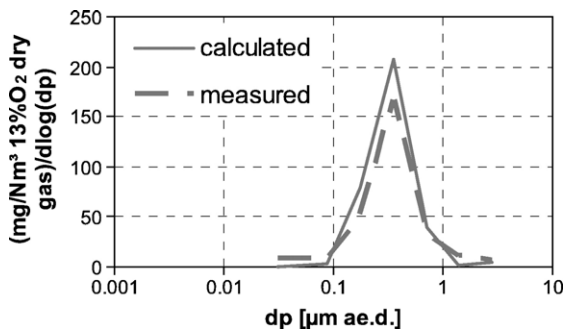


Fig. 8. Measured and calculated particle size distribution of aerosols formed during combustion of waste wood in a CHP plant at boiler outlet.

The calculated chemical compositions of aerosol particles formed during waste wood combustion (Fig. 9) are also similar to the measured chemical composition (Fig. 2), but the element concentration trends over the particle diameters are partly different. For example the concentration of Zn decreases with increasing particle diameter, which is in contradiction to the measurement results. This can be explained by the fact that the modeling calculations did not predict the formation of ZnO particles as expected from the fuel analysis and confirmed by the HTLPI measurements [3]. Instead, nucleation of alkali sulfates (K_2SO_4 , Na_2SO_4) took place with subsequent condensation of alkali chlorides (KCl, NaCl) and heavy metal compounds (PbO , $PbCl_2$, $ZnCl_2$). The reason for this deviation may be that the ZnO particles found by measurements could have formed already in the primary zone of the CHP plant from gaseous ZnO in regions, where locally oxidizing flue gas conditions prevail. The formation of gaseous ZnO cannot be predicted by performing thermodynamic equilibrium calculations since under reducing conditions, which have to be assumed in the primary combustion zone generally due to the plug flow model approach, it is no stable reaction product. A possibility to improve the calculations regarding this problem in future could be the consideration of weakly oxidizing conditions in the primary combustion zone.

The simulation of aerosol formation during co-combustion of coal and sawdust leads to a slightly different PSD than the measured one (Fig. 10). With the simulation only one submicron peak (on the second impactor stage with a cut diameter of $0.125 \mu m$ ae.d.) could be reproduced. The fact that the second peak on the fourth impactor stage (cut diameter of

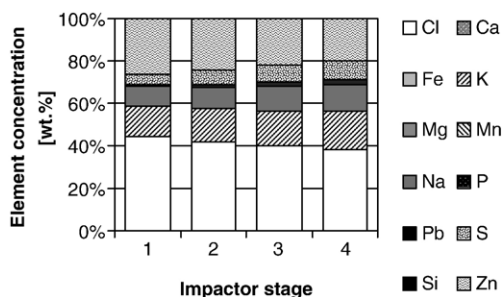


Fig. 9. Calculated particle composition of aerosols formed during combustion of waste wood in a CHP plant at boiler outlet.

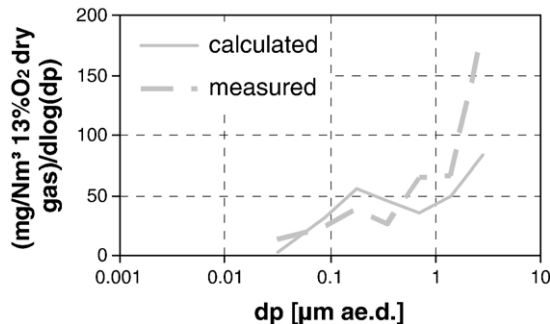


Fig. 10. Measured and calculated particle size distribution of aerosols formed during co-firing of sawdust with coal in a power plant at boiler outlet.

$0.5 \mu m$ ae.d.) could not be reproduced could on the one hand depend on the primary particle PSD, which has to be estimated in the submicron size range and on the other hand to the simulated precipitation efficiency of the respective impactor stage, which might differ from the real precipitation efficiency. The calculated total mass load of aerosols in the flue gas amounts to $52.4 mg/Nm^3$, which is a little less than the measured mass load of $55.1 mg/Nm^3$ (both values related to 13 vol.% O_2 and dry gas).

The calculated chemical compositions of aerosol particles from co-combustion of coal and sawdust (Fig. 11) show similar aerosol compositions on the single impactor stages as the measured compositions (Fig. 2). The calculated concentration trends of the single elements related to the particle diameter are the same as for the measurements except for K and Na, which can be explained with an increased condensation of K_2SO_4 and Na_2SO_4 with decreasing particle size and the rising particle surface. Moreover, the consideration of CaO as condensable compound for aerosol formation during coal combustion and biomass co-firing leads to the nucleation and accumulation of CaO in the aerosol fraction as it can be derived from the upgraded Ca concentrations on the two smallest impactor stages (cut diameters of 0.0625 and $0.125 \mu m$ ae.d.). The decreasing S concentration with increasing particle size, which can, according to the measurement results, be related to the formation of $CaSO_4$ is during modeling caused by the increased condensation of K_2SO_4 and Na_2SO_4 as mentioned.

Measurement results as well as modeling results clearly show the effect of fuel composition on aerosol amount, PSD and

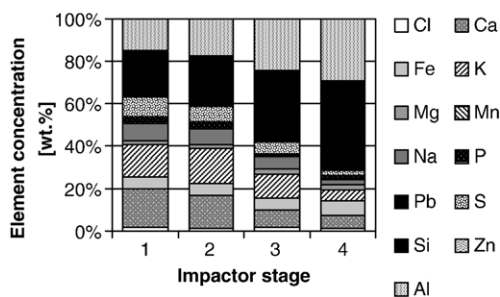


Fig. 11. Calculated particle composition of aerosols formed during co-firing of sawdust with coal in a power plant at boiler outlet.

chemical composition. Due to the fact, that three very different combustion plants were used an effect of the combustion plant on aerosol formation is most probable. The smaller temperature gradients in the CHP plant and in the power plant compared to the pilot-scale heating plant should favor the condensation of ash vapors on existing particles compared to the nucleation of new particles and result in a larger mean particle diameter. Additionally, due to the longer residence time, particle coagulation is enhanced in the in the CHP plant and in the power plant. In fact, the peaks of the particle size distributions obtained from measurements and modeling of aerosol formation in the large-scale combustion plants have a higher mean particle diameter (ae.d.). Additionally, during combustion of wood chips (spruce) nucleation of particles from ash forming vapors could be confirmed by measurements [3] and by calculations. But these effects could also be related to the different fuels used. The amounts of aerosol forming elements released to the gas phase as well as the amount of particles entrained from the fuel will affect mass load, PSD and the chemical composition of aerosols. Therefore, based on the measurements and calculations performed the effect of the combustion plant on the aerosol PSDs can therefore not be separated from the effect of the fuel composition. In order to investigate this effect, a sensitivity study of aerosol formation focusing on different time–temperature profiles has to be performed.

Furthermore, a comparison of the calculated mass load of aerosols at boiler outlet with the mass of aerosol forming elements in the gas phase at the secondary air inlet for the single combustion plants showed that the precipitated amount of aerosol forming matter in the combustion plants is for all three cases below 20%. A more detailed evaluation of the predicted precipitation of aerosol forming matter has yet to be performed.

5. Summary and conclusions

A mathematical model has been developed in order to simulate the formation and behavior of aerosol particles originating from the combustion of woody biomass fuels as well as of the co-combustion of biomass with coal in various combustion systems. This model should support the understanding of aerosol formation during biomass combustion and should clarify different formation pathways and also identify relevant influencing variables concerning aerosol formation.

The model is a one dimensional plug flow model and includes thermodynamic equilibrium calculations for the determination of the gas composition and a kinetic approach to calculate the amount of sulfates in the gas phase. Furthermore, the relevant particle formation mechanisms nucleation, condensation and coagulation as well as the particle deposition mechanisms gravitational settling, inertial impaction, thermophoresis, turbophoresis and diffusion as well as vapor condensation on furnace and boiler walls are considered. Additionally, the possibility of inserting primary particles (particles directly entrained from the fuel) in various amounts and compositions as starting values for the calculations is given.

The model was used to simulate the aerosol formation and behavior during combustion of wood chips (spruce), waste

wood and during co-combustion of coal and sawdust. The calculation results were compared with measurements of aerosol particle size distributions, aerosol mass load in the flue gas and particle compositions performed at a wood chips (spruce) fired pilot-scale heating plant equipped with a 440 kW_{th} flame tube boiler, at a waste wood fired CHP plant with a nominal boiler capacity of 40 MW_{th} and at a power plant co-firing coal and sawdust (12 wt.%) with a boiler load during the measurements of 404 MW. The aerosol measurements were performed at boiler outlet before the cyclone at the pilot-scale plant and at the CHP plant and before air preheater at the co-firing power plant.

The measurement and calculation results show that aerosol formation from chemically untreated wood chips (spruce) is not influenced by ZnO particles due to the small Zn concentrations in the fuel. Therefore, just a small amount of submicron particles originating from the entrainment from the fuel bed (consisting mainly of Ca and Si), are present in the flue gas in the furnace region and thus not enough surface is provided for suppression of particle nucleation by condensation. Subsequently, new particles form by nucleation from the ash forming vapors, which are primarily K₂SO₄ and other alkali compounds (Na₂SO₄, KCl, NaCl).

During waste wood combustion aerosols form from ZnO vapor by nucleation and condensation in the furnace, which could be confirmed by the measurements performed. During further flue gas cooling other ash forming compounds, which are alkali sulfates (K₂SO₄, Na₂SO₄), alkali chlorides (KCl, NaCl) and heavy metal compounds (PbO, PbCl₂, ZnCl₂), condense on these ZnO particles. Nucleation of new particles from alkali sulfate, alkali chloride and heavy metal compound vapors is mostly suppressed due to the surface provided for condensation by the ZnO particles. This formation pathway took not place according to the calculations, which predicted the nucleation of alkali sulfates (K₂SO₄, Na₂SO₄) and subsequent condensation of alkali chlorides (KCl, NaCl) and heavy metal compounds (PbO, PbCl₂, ZnCl₂). The reason for this deviation is that the formation of ZnO particles most probably takes place already in the primary combustion zone of the CHP plant right over the fuel bed as soon as Zn vapors released meet an oxidizing environment, which was not considered in the calculations.

Furthermore, measurements and calculations confirmed that aerosol formation during co-combustion of coal and sawdust is strongly influenced by the PSD and the chemical composition of submicron particles resulting from the defragmentation of coal ash and being entrained with the flue gas (particles consisting mainly of Al, Ca, Fe, K and Si). Additionally, due to the high temperature prevailing in the furnace during co-firing of sawdust with coal the release of Ca to the gas phase and the subsequent nucleation of CaO particles during cooling of the flue gas, which was assumed to take place according to the analysis results, could be reproduced with the calculations. Nucleation of other ash forming vapors was suppressed by these primary particles.

Moreover, the type of combustion plant (time–temperature profile of the flue gas) should have an effect on aerosol mass load, PSD and chemical composition. But due to overlaying

effects of the fuel composition, which influences the amounts of elements released to the gas phase as well as the amount and PSD of particles entrained from the fuel to the gas phase, the effects of fuel composition and of the time–temperature profile of the combustion plants on PSD, mass load and chemical composition of aerosols could not be separated and have to be investigated in a separate sensitivity study.

Finally, it can be stated that the aerosol formation model developed is mostly applicable to determine particle size distribution and chemical composition of aerosols from combustion of different woody biomass fuels and for the co-combustion of biomass fuels with coal. Moreover, the model as well as the measurement results clearly point out that different formation mechanisms of aerosols have to be considered for chemically untreated wood chips, waste wood and co-combustion of biomass with coal.

Further work on the aerosol formation model will comprise a more detailed evaluation of the probable primary particle size distributions in the submicron particle ranges as well as gas phase modeling in the primary combustion zone in order to determine the point of first ZnO particle formation. Additionally, the implementation of modeling aerosol formation and precipitation into a CFD code describing ash deposit formation is foreseen.

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