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Pagels, Joakim; Strand, Michael; Rissler, Jenny; Szpila, Aneta; Gudmundsson, Anders; Bohgard, Mats; Lillieblad, L; Sanati, Mehri; Swietlicki, Erik

Characteristics of Aerosol Particles Formed During Grate Combustion of Moist Forest Residue

J. Pagels[a,*], M. Strand[b], J. Rissler[c], A. Szpila[a], A. Gudmundsson[a], M. Bohgard[a],

L. Lillieblad[b], M. Sanati[b] and E. Swietlicki[c]

[a]Div. of Aerosol Technology (EAT), Lund University, P.O. Box 118, SE-22100, Lund, Sweden

[b]Div. of Bioenergy Technology, Växjö University, SE-35195, Växjö, Sweden

[c]Div. of Nuclear Physics, Lund University, P.O. Box 118, SE-22100, Lund, Sweden

*To whom correspondence should be addressed

E-mail: **joakim.pagels@design.lth.se**

Phone: +46 46 222 98 91, Fax: +46 46 222 44 31

Running title: Particles from grate combustion of biomass

Abstract

The characteristics of aerosol particles formed during combustion of moist forest residue were studied as a function of load in a 1 MW moving grate boiler and at almost full load in a similar larger 6 MW boiler. When the load was increased from 50% to 75%, the coarse (1 μm < d_{ae} < 10 μm) particle number and mass concentration increased by more than one order of magnitude. An increase in boiler load was also associated with a decrease in fine particle mean diameter and fine particle total volume and mass. The combined effects led to an increase in PM_{10} with increasing load. The number and mass concentration and the size distribution were similar in the two boilers when operated at high load. The dominant inorganic elements were K, S and Cl in the fine mode and Ca, K and S in the coarse mode. The dominant ions in the fine mode were K^+, SO_4^{2-} and CO_3^{2-}. The fine mode particles had hygroscopic growth factors of around 1.65 at RH=90%, with a deliquescence point at a relative humidity between 30% and 60%. It was assessed that K_2CO_3 is responsible for the low deliquescence point. Fine mode particles of a given dry diameter had similar chemical composition.

Introduction

The utilisation of biomass for energy production is expected to increase since biomass is regarded as a CO_2 neutral fuel. During biomass combustion large amounts of fine particles are being formed. In light of recent epidemiological findings, which demonstrate a correlation between increased ambient levels of PM_{10} and $PM_{2.5}$ and increased mortality and morbidity in the population, it is important to increase the knowledge of the formation mechanisms and particle emission levels from boilers with different capacities.

In Sweden it is expected that a large proportion of the increased utilisation of woody biomass fuels will be invested in power plants that produce between 0.5 and 10 MW, using moving grate technology. Today most plants smaller than 5 MW are equipped with multi-cyclones as the only measure for particle separation. Moist forest residue is a fuel, the quality of which may be too low for many residential boilers, but is suitable for boilers of the moving grate type.

Aerosol particles formed during woody biomass combustion can usually be divided into two modes (Lighty et al., 2000). The main route of particle formation for the fine mode ($d_{ae} < 1$ μm) is nucleation and condensation from the gas phase. The fine mode usually consists of particles with diameters between 50 and 300 nm and is dominated by potassium salts, with a significant heavy metal content (especially Zn, but also Cd and Pb). At a high degree of incomplete combustion the carbon content can dominate. The coarse mode ($d_{ae} > 1$ μm) is believed to mainly consist of ash residuals. It usually has a high content of low volatility metals (e.g. Ca, P and Si), along with K and S.

Most of the knowledge concerning particle formation is retrieved from measurements in Circulating Fluidised Bed (CFB) combustion in larger plants. Valmari et al. (1998) found that during combustion of willow, K_2SO_4 condenses at temperatures above 650° C, while KCl condenses below 650° C. When a stochiometric excess of positive ions was detected, it was assessed from thermodynamic equilibrium calculations that the excess potassium condensed as K_2CO_3. During CFB combustion of moist forest residue Valmari et al. (1999) found that the particle phase sulphur and metals were to a large extent associated with the coarse mode, probably due to surface reactions during oxidising conditions.

Jokiniemi et al. (2001) used a numerical code to model the aerosol dynamics during fluidised bed combustion. They found that the condensation of volatile species (e.g. Cl and Pb) on the coarse mode is insignificant and the presence of these elements in the coarse mode instead may be explained by non-complete vaporisation, chemical surface reactions or re-entrainment of deposited particles.

Moisio (1999) performed extensive realtime characterisation of particles formed during CFB combustion of different biofuels using an Electrical Low Pressure Impactor (ELPI). In all the CFB studies mentioned here, the coarse mode dominated the mass particle size distribution up to 10 µm ($PM_{1-10} > PM_1$) downstream of the heat exchanger.

The composition of particles emitted from residential boilers is often dominated by organic and black carbon. The coarse mode is generally absent (Johansson, 2002). Christensen et al. (1998) and Livbjerg (2001) found that the fine particle formation during combustion of straw is determined by kinetically limited SO_2 oxidation.

The fuel introduced into a CFB boiler and a moving grate boiler will have substantially different time-temperature histories. The fuel introduced into the CFB boiler will experience an intense heat exchange with the gas and the bed material, and it will be quickly dried, heated and combusted. The bed temperature during CFB combustion is comparatively low ~800-900 °C. This is opposed to the process in the moving grate boiler, where the introduced fuel will be slowly heated dried and pyrolysed as it is transported down the grate. Finally the char will be combusted at high temperatures (~1000-1100° C). This difference in temperature will have a considerable influence on the volatilisation of particle forming pre-cursors.

There is some data available concerning particle formation and emissions during moving grate combustion of bio fuels. Hasler and Nussbaumer (1998) used an Andersen cascade impactor during combustion of three different fuels. The fine mode dominated the mass, except for the bark fuel for which a coarse mode (~50% of the mass) was found. Obernberger et al. (2001) performed extensive characterisation of various woody biofuels in a pilot-scale (0.4 MW) boiler. They used a low-pressure cascade impactor. A dominating fine mode (PM_1 >90% of PM_{10}) by mass, with an

aerodynamic mean diameter between 0.1 and 0.5 μm was found in all cases. The fine mode mass varied between 20 –150 mg/m^3 (13% vol. O_2 dry) and was highly correlated with the K, S and Cl content of the fuel. A larger total fine particle mass was associated with an increased particle mean diameter. The particle mass measured as total dust increased with increasing boiler load.

Moving grate systems are often used from very low (~10-20%) to full load due to the sharply varying energy demands. Johansson et al. (2001) used an ELPI to study particle number size distribution together with total dust measurements in two moving grate boilers. They found that the fine particle diameter increased and the particle number decreased at lower load. The total fine particle volume or mass was not reported.

The interaction between the emitted aerosol particles and water vapour may be of importance, e.g. regarding climate effects, respiratory deposition and wet flue gas cleaning techniques. Using a Hygroscopic - Tandem Differential Mobility Analyser (H-TDMA), the particle hygroscopic growth during subsaturation can be studied. The growth factor (G_F) is defined as the droplet diameter at the considered RH divided by the diameter at low RH (typically below 10%).

Weingartner et al. (1997) showed that freshly produced diesel particles have very low hygroscopic growth factors close to 1.0 when exposed to a RH up to 99%. Dua and Hopke (1996) showed that particles from a residential wood stove with flames burning had growth factors close to 1.0 at RH~99%. However, during smouldering growth factors of around 2.0 were reported.

The overall aim of this work was to study the concentrations and characteristics of aerosol particles from moving grate combustion of moist forest residue. The main part of the study is based on measurements at different load in a boiler with a maximum thermal output of 1 MW. The majority of the measurements were sampled downstream the multi-cyclone (the only flue-gas cleaning system). For comparison, data from a similar larger 6 MW unit operated at high load is included.

Particle number concentrations and size distributions were studied using on-line particle spectrometers, a Scanning Mobility Particle Sizer (SMPS) and an Aerodynamic Particle Sizer (APS). A H-TDMA was used to study the fine particle hygroscopic properties and mixing status. Two off-line analytical methods, Particle Induced X-ray Emissions (PIXE) and Ion Chromatography (IC) were used to determine the chemical composition of samples size segregated using a Low-Pressure

Cascade Impactor (DLPI) and a Stacked Filter Unit (SFU). Mass weighted size distributions were determined gravimetrically from the DLPI-samples.

Methods

Description of the combustion system

The two utility boilers are located in the southeastern part of Sweden. An outline of the combustion system in the 1MW boiler is presented in Fig. 1.

Figure 1.

The fuel is fed into the combustion chamber using a conveyor screw. The fuel is dried, pyrolysed and the char is finally combusted during transport on the moving grate. The primary air, supplied through the grate is taken from the air above the boiler. The boiler load regulates the flow of primary air. In the 1 MW boiler, the only measure for flue gas cleaning is a multi-cyclone, while the larger boiler is also equipped with an electrostatic precipitator (ESP) down-stream of the cyclone. In the larger unit there is a flue gas condenser downstream of the ESP, the condenser has a maximum thermal output of 1.5 MW.

The fuel used in both plants was moist forest residue. It mainly consisted of branches and treetops, which were by-products of the timber processing in the forest. The fuel consisted of a relatively large fraction of bark. The dominant species were spruce and pine.

Two samples for fuel and ash analysis were taken in the 1 MW boiler. The amount of sulphur (method: ASTMD4239) and chlorine (method: ASTMD4208) in the fuel samples was determined. The fuel was ashed at 575° C and the elements in the ash were determined using X-Ray Fluorescence semi-quantitative analysis. The analysis of the fuel and the fuel ash is given in Table 1.

Table 1

The flue gas particles were sampled upstream and downstream of the multi-cyclone in the 1 MW boiler and downstream the multi-cyclone in the 6 MW boiler. The flue gas temperature was 150-215° (depending on boiler load). All number and mass concentrations were converted to 13% CO_2 dry gas at normal temperature (0 °C) and pressure (101.3 kPa).

Particle Sampling and Analysis

An outline of the sampling system is given in Fig. 2. The flue gas sample was taken isokinetically from the middle of the flue gas duct using a thin-walled probe. The sample was diluted with filtered and dried air in the primary dilution system. The diluter was designed to induce turbulent flow to ensure fast mixing. A primary dilution factor of 1:10 (nominal) was used in the 1 MW boiler and 1:20 (nominal) in the 6 MW boiler.

The dilution and outlet excess airflows were regulated using calibrated Mass Flow Controllers (MFC). The flows of the MFC's were balanced to zero sampling flow according to the pre test calibration. The desired dilution ratio was established by further increasing the outlet excess flow. This point of zero sampling flow was verified routinely by noting the point when the APS (model 3320, TSI Inc., US) started to detect particles. The dilution ratio was verified using measurements of O_2 in the dilution air and the diluted sample.

Figure 2.

A cyclone was used in the experimental set-up to remove large particles. The cyclone was designed for 50% aerodynamic cut-off diameter at 10 μm ($d_{ae,50}$=10 μm). The total flow rate through the sampling system was 40 l min^{-1}. The residence time in the system from dilution to the splitter before the instruments was about 4 s. The flow was split to the different instruments using isokinetic sampling. Penetration of particles (>1 μm) from the inlet of the thin-walled probe to the output of the splitter, including the cyclone was determined experimentally at ambient conditions in a laboratory using an APS (model 3310, TSI Inc.). The method was similar to that described by Gudmundsson and Lidén (1998). The results are given in Fig. 3. The fitted penetration curve was used to correct the DLPI data for particle losses in the sampling system.

Figure 3.

An electrical mobility spectrometer (SMPS 3934, TSI Inc.), incorporating a Condensation Particle Counter (CPC model 3022, TSI Inc.), was used to determine the number particle size distributions in the range 17-550 nm. In order to operate the CPC in the counting mode the flue gas sample was secondary diluted with a factor 1:10 using an ejector diluter (model VKG 10,

Palas GmbH). The artefacts induced by the relatively long CPC-response time were minimised using scan times of 240 s up and 120 s down.

The particle hygroscopic properties were studied at subsaturation using a H-TDMA (Swietlicki et al., 1999). In this set-up monodisperse dried particles (RH<10%) were extracted from the first DMA. The aerosol flow from DMA1 was then humidified to a known RH. The particle size spectrum of the grown particles was studied using the second DMA. The system was operated at a RH of 90% (nominal). Hygroscopic growth factors were determined for particle diameters between 35 and 350 nm. Separate series of scans at a constant dry diameter, where the RH was varied in steps from 25% to 90%, were used to evaluate the deliquescent behaviour of the flue gas particles. Separate measurements were performed in a laboratory with pure K_2SO_4 and K_2CO_3. The system was calibrated using $(NH_4)_2(SO_4)$.

An APS 3320 was used to determine the number particle size distribution of coarse particles (1-10 μm). The instrument was used in the correlated mode throughout the majority of the measurements. Each sample was 180 or 360 s long.

A 13-stage low-pressure multi-jet cascade impactor (DLPI, Dekati Ltd., Finland) was used to determine the mass weighted size distribution in the range 30 nm to 10 μm. Samples were taken for time periods of 10 to 20 minutes, resulting in a maximum collected mass of less than 0.4 mg per stage. Polycarbonate capillary pore filters (Nuclepore, Whatman Inc., UK) were used as substrates. The substrates were coated with high vacuum grease. The samples were heated in an oven to 125° for at least 5 h both prior to and after sampling. All gravimetric analyses were performed at a relative humidity below 30%.

Samples were also taken using a Stacked Filter Unit (SFU). The SFU consists of two capillary pore filters (Nuclepore) connected in series (Heidam, 1981). The pore size in the first filter is 8 μm with high transmission for fine particles. The second filter has a smaller pore size (0.4 μm) ensuring an effective collection of the fine particles.

The DLPI and SFU samples were analysed for 30 elements (Z>12) using PIXE analysis. Water-soluble positive and negative ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^- and NO_3^-) on the

SFU substrates and selected halves of the DLPI substrates were determined using Ion Chromatography (IC).

Measurement plan

The field investigation at the 1 MW boiler was carried out in February 2001 and covered detailed investigation during 5 days. During day I and II, the main focus of the investigation was to study the particle hygroscopic properties. During day III measurements were taken at 45% load. On day IV, measurements were taken at two different boiler loads (50 and 75%). During day V, particles were sampled before the multi-cyclone. The O_2 level was $9.0\pm0.5\%$ (dry flue gas) and the oven temperature was 1050 ± 10 °C throughout the 5 days of measurement. The CO and NO concentrations were measured on a separate day at loads between 45 and 60%. The baseline of the CO concentration was 25 ppm, peak values of 40-150 ppm (sampling frequency 6 Hz) were obtained during grate movements every 2-3 minutes. The NO concentration was 160-180 ppm.

The field investigation at the 6 MW boiler was carried out in March 2001. The main focus of the measurements was to investigate the particle separation efficiency of the ESP and the flue gas condenser. These results are reported elsewhere (Strand et al., 2002). In this paper only measurements downstream the multi-cyclone are reported. The flue gas re-circulation was in use. The hourly mean of the O_2 level varied between 5.5 and 6.2% during the measurement period. The oven temperature was 1050 °C. The CO concentration varied between 45 and 185 ppm. The NO concentration varied between 107 and 123 ppm.

Results and Discussion

Particle Size and Concentration Measurements

During the first 3 days of measurements in the 1 MW boiler it was found that the boiler load had a considerable influence on the particle emissions (Table 2). The given data in Table 2 are mean values of 2 h or more during nearly stable operating conditions. In order to minimise the influence of heterogeneities in the fuel, comparisons with the settings at two different boiler loads were performed

on the same day (day IV). The load of the plant was lowered manually to around 50% (Fig. 4) for a period of 3 h (denoted day IV_a). At 14.30 hrs, the load was again regulated by the local energy demand and increased to a mean level of 75% (denoted day IV_b).

Table 2.

Time series from day IV for the total number of coarse particles, total number of fine particles and geometric mean diameter (GMD) of the fine particles are given in Fig. 4. Note the almost twenty-fold increase in total coarse particle number > 1 μm determined by the APS. Even the small peaks in load at just before 16.00 hrs and at 18.00 hrs are clearly evident as peaks in the coarse number concentration. The fine particle number remained close to constant, while a decrease in GMD was found, when the load was increased. The findings at different load during day IV_a and IV_b were in good agreement with the day-to-day variations observed during day I to III.

Figure 4.

The number size distribution measured with the SMPS-system was mainly unimodal during the whole measurement period. However, a weak nucleation mode at around 40 nm, which fluctuated over time, could be distinguished. This mode had its largest contribution during day II (Fig. 5). Analysis of the raw data from the CPC showed that the data points above 400 nm are overestimated due to the relatively slow response time of the CPC 3022.

Figure 5.

In Fig. 6, the coarse particle size distribution is given for day IV, the measurements taken during day V upstream the multi-cyclone and the measurements in the 6 MW boiler. Each point represents the mean of four APS channels. The dramatic difference between the 50% and 75% load setting can be seen again. The measurements taken in the larger boiler are in the same range as those taken at 75% load in the 1 MW boiler. The concentrations measured before the cyclone at 60% load is in the range of the low load data for the smaller particles, but increases with increasing diameter. This increase may represent particles that are collected in the multi-cyclone.

Figure 6.

Figure 7.

In Fig. 7, the gravimetric analyses of the four samples taken with the DLPI are presented. The coarse fraction, PM_{1-10} contributed to more than 50% of the particle mass emitted as PM_{10} during sample IV_b (Table 3). However, this sample was taken just before 16.00 hrs when the concentration of the coarse particles reached its highest peak during the day according to the APS measurements. The sample taken in the corresponding position in the larger boiler shows a similar distribution between the fine and the coarse mode. However, during sample III and V in the smaller boiler at lower load, the coarse mode (PM_{1-10}) contributed to less than 5% of PM_{10}. This difference in coarse mode concentration is in good agreement with the data taken simultaneously with the APS. There was an increase in PM_{10} at higher load due to the sharp increase in coarse mode concentration. Note that PM_{10} was totally dominated by PM_1 *before* the multi-cyclone during sample V.

Table 3.

When increasing the load, the primary air taken through the grate is increased; this itself may lead to a higher potential of the air stream to carry coarse particles away from the combustion zone. Separate studies of the fuel bed in the 1 MW boiler showed that inhomogeneities might form in the bed in certain circumstances. This may explain the sharp increase in concentration of the coarse particle mode. Another possible explanation is that the coarse Ca-rich particles are less efficiently fragmented at lower load. If the Ca-rich particles are larger than 10 μm they are beyond the measurement range in this study, but would be efficiently removed by the multi-cyclone or trapped in the bottom ash.

The lower coarse mode concentration found by other investigators may be due to different fuels, different combustion systems or better optimised multi-cyclones, but may also be caused by an-isokinetic sampling or due to errors when correcting for particle losses in the sampling system.

The decreased fine mode mean diameter at higher load can partly be explained by a lower degree of particle coagulation, as the residence time in the boiler system is shorter at the higher load. Further, the temperature gradient in the heat-exchanger area is larger, which may influence the nucleation and subsequent condensation. The decrease in particle diameter leads to a decrease in the

assessed particle volume ($PV_{0.55}$) from the SMPS measurements. The PM_1 determined from the DLPI samples also suggested a similar trend.

The components volatilised in the combustion process may end up in four different ways:

1) As fine particles formed from nucleation and condensation.

2) As coarse particles through condensation, chemical reactions, coagulation (via the fine mode) or from re-entrainment of particles deposited on the flue gas channel walls.

3) As deposit on the walls of the flue gas channels (especially in the heat exchanger area) either from the gas or particle phase.

4) Remain in the vapour phase.

As can be seen even if the volatilised mass is the same it is very difficult to predict what mechanism is the cause for the changes in fine particle volume/mass. Based on this data set it can not be proven that the decrease in fine particle volume/mass is caused by volatilised material ending up in the coarse mode due to mechanism 2, when the high concentration of coarse particles are present.

As no carbon analysis was made in this study it can generally not be ruled out that the increased fine particle volume was caused by a larger amount of elemental or organic carbon present in the particles for the low load case. The total PAH concentration (particle and gas phase) of 29 analysed compounds was only 2.8 $\mu g/m_n^3$ at medium load (65%) indicating that the carbon content was low (Lillieblad et al., 2003). Another uncertainty is the particle shape.

Particle Chemical Composition

The four most abundant elements as determined by PIXE are shown in Fig. 8 for one DLPI sample from each plant. The samples are not directly comparable especially for the coarse mode, as the 1 MW boiler was operated at 45% load and the 6 MW boiler was operated at 85% load. The most abundant elements analysed in the fine mode were K, S and Cl and in the coarse mode Ca, K and S. Note the very low concentration of Ca in the fine mode and how the Cl concentration relative to S decreases with increasing particle diameter.

Figure 8.

During CFB combustion of forest residue (Lind et al., 1999), S, Pb, Zn and Cd were almost entirely associated with the coarse mode. In the 6 MW boiler these elements were to a larger extent associated with the fine mode. Pb was almost entirely associated with the fine mode, while S, Zn and Cd were more evenly distributed indicating a partial evaporation or chemical reaction with the coarse mode. This is expected as the temperature is higher leading to a higher degree of evaporation during grate combustion compared to CFB combustion. The elemental concentration as a function of particle diameter in the 6 MW boiler is described in more detail by Strand et al. (2002).

An excess of positive ions was determined from the 7 ions detected with IC. We made the assumption that the undetected negative ions were solely CO_3^{2-} and undetected positive ions were negligible. According to thermodynamic equilibrium models, excess K would condense as K_2CO_3. In Fig. 9 a summary of the IC analyses is given, ion equivalent concentrations are used. It can be seen that K^+ constituted around 90% of the positive ions. Na^+ was the second most abundant positive ion in the 1 MW boiler, while Mg^{2+} was the second most abundant positive ion in the impactor sample taken in the 6 MW boiler. SO_4^{2-} constituted around 50% of the negative ions. The assessed level of CO_3^{2-} was on average as high as 40%, while the Cl^- level was around 10% of the detected negative ions. The increase in S/Cl ratio with increasing particle diameter can also be seen in the IC analysis.

Figure 9.

Hygroscopic Growth Measurements

During day I and II, the particle hygroscopic properties were studied using the H-TDMA. In Fig. 10 the hygroscopic growth factors at RH=90% as a function of particle diameter is given. The particle growth factors were around 1.65 at 100 nm (dry diameter).

At each particle dry size measured, all particles had similar hygroscopic properties at a specific time. The humidified size distribution was unimodal and the variability at a given dry size was only slightly larger than that for pure salts. This suggests that the processes of nucleation, condensation and coagulation shape the particles into an internal mixture. That is particles of a given

dry size have similar chemical composition. The spread in growth factor for a given diameter in Fig. 10 represents variations in the combustion process over time.

Figure 10.

The results of the deliquescence scans from day II in the 1 MW boiler are given in Fig. 11. Two series of scans at dry diameter 200 nm and one scan at 120 nm is included together with the results for pure K_2SO_4 and K_2CO_3. The flue gas particles started to take up water between RH = 30 and 60%. For K_2SO_4 we determined a deliquescence point as high as RH~98%. However, K_2CO_3 which has a higher solubility started to take up water already at around RH=30%. The modelled deliquescence point of KCl is RH=80% (Tang 1997). During day II the assessed equivalent ion concentration was around 50% CO_3^{2-}, 40% SO_4^{2-} and 10% Cl^- for negative ions.

Figure 11.

The hygroscopic growth factors of the flue gas particles at RH=90% were lower than for pure K_2CO_3 and KCl. This may be due to the high content of K_2SO_4 or due to less hygroscopic compounds, e.g. elemental or organic carbon. In a mixed particle it is likely that K_2SO_4 contributes to the hygroscopic growth below its deliquescence point. However, the influence of K_2SO_4 on the growth factors of a mixed particle needs to be further addressed.

The slight decrease in growth factor with increasing diameter suggests that particles of different size have slightly different chemical composition. This is not surprising as the smallest particles detected with the H-TDMA (35 and 50 nm) to a large extent belonged to the nucleation mode.

Christensen et al. (1998) noted that submicrometer particles from combustion of straw took up water vapour from the air in the laboratory only for the samples when there was a stochiometric excess of K^+ compared to SO_4^{2-} and Cl^- as detected by IC. They attributed this to the possible presence of KOH in the samples. KOH is even more hygroscopic than K_2CO_3.

Johansson (2002) used a semi-quantitative method, Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) to determine the alkali ions in DLPI samples of submicrometer particles from residential and moving grate combustion of three different fuels. She found that K_2CO_3

contributed 1-24% of the alkali salts by mass in 10 samples. OH$^-$ was noted as detected but not quantified.

Instrumental Issues

The water uptake at low RH is a potential source for measurement errors in particle size measurements. The DLPI sampling in the 1 MW plant was performed at RH=50-75% and the size distribution measurements may have been slightly affected by hygroscopic growth. The SMPS sample on the other hand was diluted a second time (1:10) with dry air, therefore no particle growth was expected. This study also demonstrates the need to perform gravimetric analysis at a low controlled relative humidity. The influence of hygroscopic water uptake on our gravimetric determination was negligible as the samples where weighted at RH<30%.

In the primary dilution unit, there is a transient water condensation on the particles. However, turbulent mixing ensures that the particles are exposed to sub-saturation conditions almost instantly upon dilution. The advantage with this kind of dilution system compared to heated primary dilution is that the dilution is more representative for the dilution process in the plume after the stack. The transient water condensation will cause the particles to collapse into more compact structures (Weingartner et al. 1997 and Rissler et al. 2003).

Heated primary dilution on the other hand prevents water and condensable material to condense on the particles, which often results in complex aggregates. The heated dilution gives more control over changes in the particle size distribution and may be desirable when one want to characterise the particles "as is" at the sampling point and generally in situations were there are high concentrations of condensable species (e.g. organic carbon) present. However when the interest is in the particles emitted to ambient air, the dilution technique used here may be more desirable.

We found a weak nucleation mode around 30-40 nm. However, Hedberg et al. (2002) used a similar dilution system when studying particles emitted from a residential wood stove. They found a nucleation mode of around 50% of the total particle number during the intermittent phase, while during the start-up phase the particle number was dominated by the nucleation mode. Future

studies needs to validate what dilution systems are most relevant when sampling particulate emissions from wood combustion of different kind.

In any dilution system thermophoretic losses occur during the cooling of the sample, this has been little studied and is not taken into account here. The secondary dilution occurs in an ejector diluter. While significant losses are expected for supermicrometer particles, the SMPS and H-TDMA systems used after the ejector diluter only operates below 550 nm. A size range in which, losses are believed to be insignificant due to the short residence time in the diluter.

When estimating the mass from the APS measurements, the agreement with the DLPI data was generally poor. The APS 3320 underestimated the mass by a factor of three to seven. We used the APS 3320 in the correlated mode, as it, according to the manufacturer would enable us to remove false counts induced by recirculation of particles in the sensor of this particular model. However, Armendariz and Leith (2002) showed that there is a significant particle count loss in the correlated mode. Using their data it was assessed that the correlated mode underestimated the number concentration by 50% at the lowest concentration in this study. Another uncertainty when estimating the mass from an APS measurement is the particle shape. Coarse particles from biomass combustion have been reported to be strongly irregular (Valmari et al. 1998 and Johansson 2002)

No samples from the SFU 1st stage (coarse fraction) were reported in this paper as PIXE analysis of two of the first stage substrates showed that there was an unexpected high degree of fine mode material deposited, possibly due to relatively high mass loading on the first stage substrate. However, in the second stage the Ca content was < 10% of the total Ca. This can be taken as an indication that coarse mode penetration to the second stage was insignificant.

Conclusions

This study demonstrated how small changes in the boiler operating parameters can have a large influence on the particle emissions released during biomass combustion in grate boilers.

The coarse mode (1-10 μm) number and mass concentrations increased by more than one order of magnitude when the boiler load was increased from 50% to 75%. The coarse and fine mode mass was of equal magnitude downstream the multi-cyclone when the boilers were operated at

higher load. The total number and total mass concentrations (PM_{10}) were similar in the two boilers. In the measurements at lower load both *before* and after the multi-cyclone it was found that PM_1 dominated PM_{10}. This suggests that with minor optimisation it may be possible to minimise the coarse mode from the combustion process itself.

Our results of the coarse mode concentration is much lower than those obtained in CFB combustion downstream the heat exchanger. The very low coarse mode concentrations found during low load are comparable to those obtained in residential boilers.

The fine mode mass (PM_1) and assessed volume ($PV_{0.55}$) decreased when the boiler load was increased. It needs to be further addressed whether this is directly caused by the large increase in the coarse mode mass.

The dominant inorganic elements in the fine mode were K, S and Cl and in the coarse mode Ca, K and S. The dominant species given as ions in water solution were K^+, SO_4^{2-} and CO_3^{2-}. The CO_3^{2-} concentration was assessed from a detected excess of positive ions.

A low deliquescent point together with thermodynamic equilibrium modelling supports the fact that CO_3^{2-} was a major constituent. The hygroscopic growth factor at RH=90% was around 1.65. At a given time particles of a given size had similar chemical composition. A slight shift in hygroscopic growth over time and for different particle diameters within the fine mode, suggests that there was a corresponding shift in chemical composition.

The relatively high hygroscopic growth factor and low deliquescence point determined may have important implications for climate effects, respiratory deposition, measurement techniques, wet flue gas cleaning methods and corrosive behaviour of particle deposits within the boiler.

Several relations that need to be further addressed were identified: The influence of the primary to secondary air ratio on the coarse mode emissions, the influence of the dilution properties on the particle size distribution and morphology. As a complement to the inorganic analyses used in this study, carbon analysis (e.g. EC/OC) is needed to better understand variations in emitted particle volume/mass at different operating parameters. A better understanding of these relations is needed in order to provide opportunities to design combustion facilities and procedures for minimal health and environmental impacts of the utilisation of biomass combustion for energy production.

Acknowledgements

References

Armendariz, A. J., & Leith, D. (2002). Concentration measurement and counting efficiency for the aerodynamic particle sizer 3320. *J. Aerosol Sci., 33,* 133.

Christensen, K. A., Stenholm, M., & Livbjerg, H. (1998). The formation of submicron aerosol particles, HCl and SO_2 in straw fired boilers. *J. Aerosol Sci., 29,* 421.

Dua, S. K., & Hopke, P. K. (1996). Hygroscopic growth of assorted indoor aerosols. *Aerosol Sci. and Techn., 24,* 151.

Gudmundsson, A., & Lidén, G. (1998). Determination of cyclone model variability using a time-of-flight instrument. *Aerosol Sci. & Techn., 28,* 197.

Hasler, P., & Nussbaumer, T. (1998). Particle size distribution of the fly ash from biomass combustion. In: *Proc. 10th European Conference and Technology Exhibition, June 8 - 11 1998,* Würzburg, Germany, pp. 1330-1333.

Hedberg, E., Kristensson, A., Ohlsson, M., Johansson, C., Johansson, P-Å., Swietlicki, E., Vesely, V., Wideqvist, U., & Westerholm, R. (2002). Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmos. Env.*, *36,* 4823.

Heidam, N. Z. (1981). Review: aerosol fractionation by sequential filtration with nuclepore filters. *Atmos. Env.*, *15,* 891.

Johansson, L. S., Tullin, C., & Leckner, B. *(2001).* Particulate emissions from small-scale biomass combustion, In: *Aerosols from Biomass Combustion, ISBN 3-908705-00-*2 (Edited by Nussbaumer, T.), pp. 87.

Johansson, L. S. (2002). Characterisation of particle emissions from small-scale biomass combustion. Licentiate Thesis, *Chalmers University of Technology,* Gothenburg, Sweden.

Jokiniemi, J. K., Lind, T., Hokkinen, J., Kurkela, J., & Kauppinen, E. I. (2001). Modelling and experimental results on aerosol formation, deposition and emissions in fluidised bed combustion of biomass, In: *Aerosols from Biomass Combustion, ISBN 3-908705-00-*2 (Edited by Nussbaumer, T.), pp. 31.

Lighty, J., Veranth., M., & Sarofirm, A. F. (2000). Combustion aerosols: factors governing their size and composition and implications for human health. *J. Air and Waste Manage. Assoc., 50,* 1565.

Lillieblad, L., Szpila, A., Strand, M., Pagels, J., Rupar-Gadd, K., Gudmundsson, A., Swietlicki, E., Bohgard, M., & Sanati, M. (2003). Boiler operation influence on the emissions of submicron particles and PAHs from biomass fired grate boilers. Submitted to *Energy and Fuels*

Lind, T., Valmari, T., Kauppinen, E. I., Sfiris, G., Nilsson, K., & Maenhaut, W. (1999). Volatization of the heavy metals during circulating fluidised bed combustion of forest residue. *Env. Sci. & Techn., 33,* 496.

Livbjerg, H. (2001). Aerosol formation forom straw combustion, In: *Aerosols from Biomass Combustion, ISBN 3-908705-00-*2 (Edited by Nussbaumer, T.), pp. 29.

Moisio, M. (1999)- Real-time size distribution measurement of combustion aerosols, PhD Thesis, *Tampere University of Technology,* Tampere, Finland, Publication 279.

Obernberger, I., Brunner., T., & Jöller., M. (2001). Characterisation and formation of aerosols and fly-ashes from fixed-bed biomass combustion, In: *Aerosols from Biomass Combustion, ISBN 3-908705-00-*2 (Edited by Nussbaumer, T.), pp. 69.

Rissler, J., Szpila, A., Lillieblad, L., Strand, M., Pagels, J., Swietlicki, E., Bohgard, M., & Sanati, M. (2003). Hygroscopic behaviour of flue gas particles emitted from a 1.5 MW biomass fired grate boiler. Submitted to the *European Aerosol Conference 2003* in Madrid, Spain.

Strand, M., Pagels, J., Szpila, A., Gudmundsson, A., Bohgard, M., Swietlicki, E., & Sanati, M. (2002). Fly ash penetration through electrostatic precipitator and flue gas condenser in a 6 MW biomass fired boiler. *Energy and Fuels, 16,* 1499-1506.

Swietlicki, E., Zhou, J., Berg, O. H., Martinsson, B. G., Frank, G., Cederfelt, S. I., Dusek, U., Berner, A., Birmili, W., Wiedensohler, A., Yuskiewicz, B., & Bower., K. N. (1999). A closure study of sub-micrometer aerosol particle hygroscopic behaviour. *Atmos. Res., 50,* 205.

Tang, I. N. (1997). Thermodynamic and optical properties of mixed-salt aerosols of atmospheric importance. *J. Geophys. Res., 102,* 1883.

Valmari, T., Kauppinen, E. I., Kurkela, J., Jokiniemi, J. K., Sfiris, G., & Revitzer, H. (1998). Fly ash formation and deposition during fluidised-bed combustion of willow. *J. Aerosol Sci., 29,* 445.

Valmari, T., Lind, T. M., Kauppinen, E. I., Sfiris, G., Nilsson, K., & Maenhaut, W. (1999). Fly ash formation and deposition during fluidized bed combustion of biomass 2. Ash deposition and alkali vapor condensation. *Energy & Fuels, 13,* 390.

Weingartner, E., Burtscher, H., and Baltensperger, U. (1997). Hygroscopic properties of carbon and diesel soot particles. *Atmos. Env., 31,* 2311.

Table 1. Fuel and ash analysis of the moist forest residue combusted in the 1 MW boiler

	Day IV	Day V
Ash 575°C (% d_b)	2.15	2.25
S (% d_b)	0.04	0.04
Cl (% d_b)	0.012	0.015
Na_2O (% of ash)	0.8	0.5
K_2O (% of ash)	14.1	10.9
CaO (% of ash)	35.7	42.7
MgO (% of ash)	5.2	3.7

Table 2. Particle characteristics mean values for periods longer than 2 h during stable conditions. The arithmetic standard deviations (of the distributions) of the measured values are given.

Measurement: 1 MW: Day I-V 6 MW: 1 Day	Load (%)	Total number, 17-550 nm ($cm_n^{-3} *10^{-7}$)	GMD Number, 17-550 nm (nm)	Total volume, 17-550 nm (mm^3/m_n^3)	Total number, 1-10 μm (cm_n^{-3})
I	100	6.3 ±0.7	87 ±4	44 ±3	6100 ±2000
II	45	5.1 ±0.6	113 ±3	77 ±10	170 ±120
III	45	5.5 ±0.5	111 ±4	84 ±8	100 ±20
IV_a	50	4.7 ±0.4	104 ±3	59 ±4	150 ±80
IV_b	75	5.1 ±0.3	90 ±3	44 ±4	2700 ±1300
V[*]	60	6.8 ±1.0	93 ±3	68 ±8	270 ±190
6 MW	85	4.4 ±0.5	83 ±3	31 ±6	4800 ±1200

* Sampled upstream the multi-cyclone.

Table 3. Mass concentrations determined with the DLPI, given as size fractions. Averages of simultaneous SMPS and APS samples are included for comparison.

Measurement: 1 MW: Day I-V 6 MW: 1 Day	Load (%)	PM_1, DLPI (mg/m_n^3)	$PV_{0.55}$, SMPS (mm^3/m_n^3)	PM_{1-10}, DLPI (mg/m_n^3)	Nbr. >1 μm, APS (cm_n^{-3})	PM_{10}, DLPI (mg/m_n^3)
III	45	117	74	5.1	200[*]	122
IV_b	80	100	48	118	5200	218
V	60	145	63	5.3	210	150
6 MW	85	79	31	78	5400	157

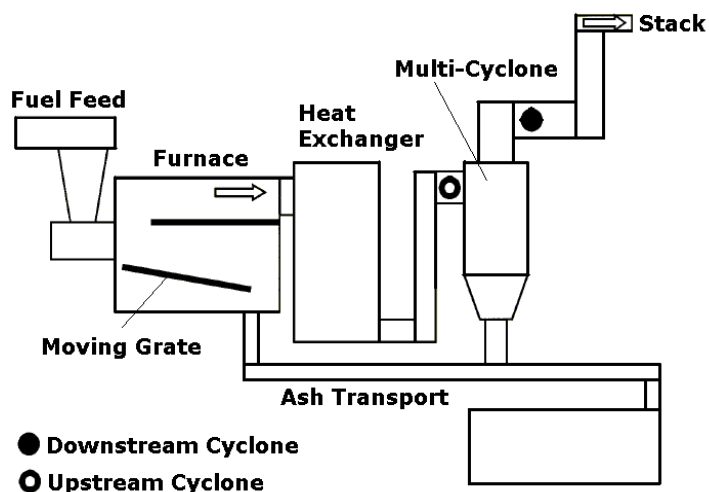*Measured in the summing mode

Fig. 1. 1 MW Grate Fired Boiler. Sampling was performed before and after the multi-cyclone.

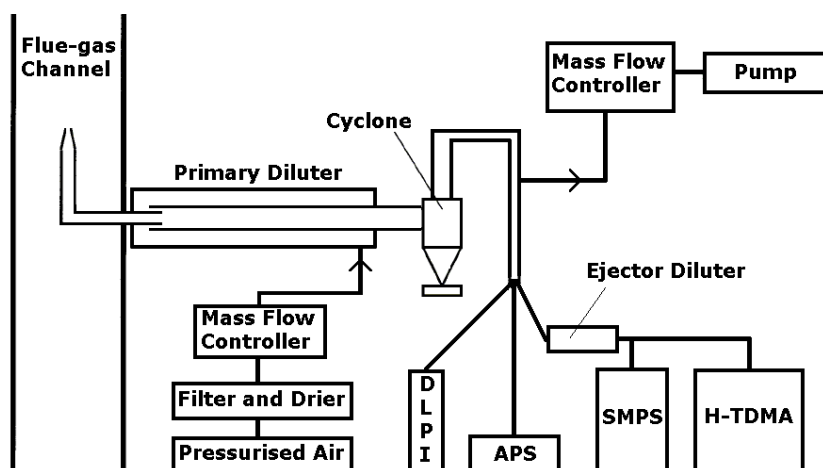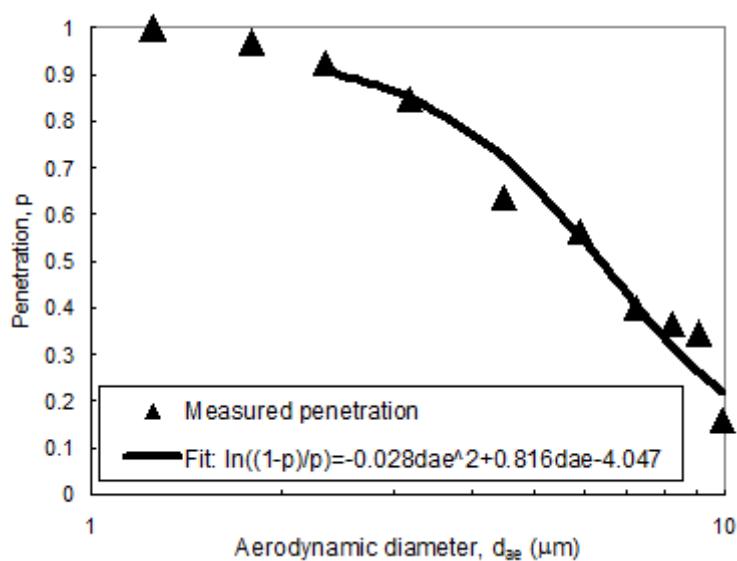

Fig. 2. Experimental set-up.

Fig. 3. Experimentally determined penetration through the sampling system. The fit was applied in the range p<0.92 (Gudmundsson and Lidén, 1998). The penetration was assumed to be 1.0 at d_{ae}=1.25 µm.
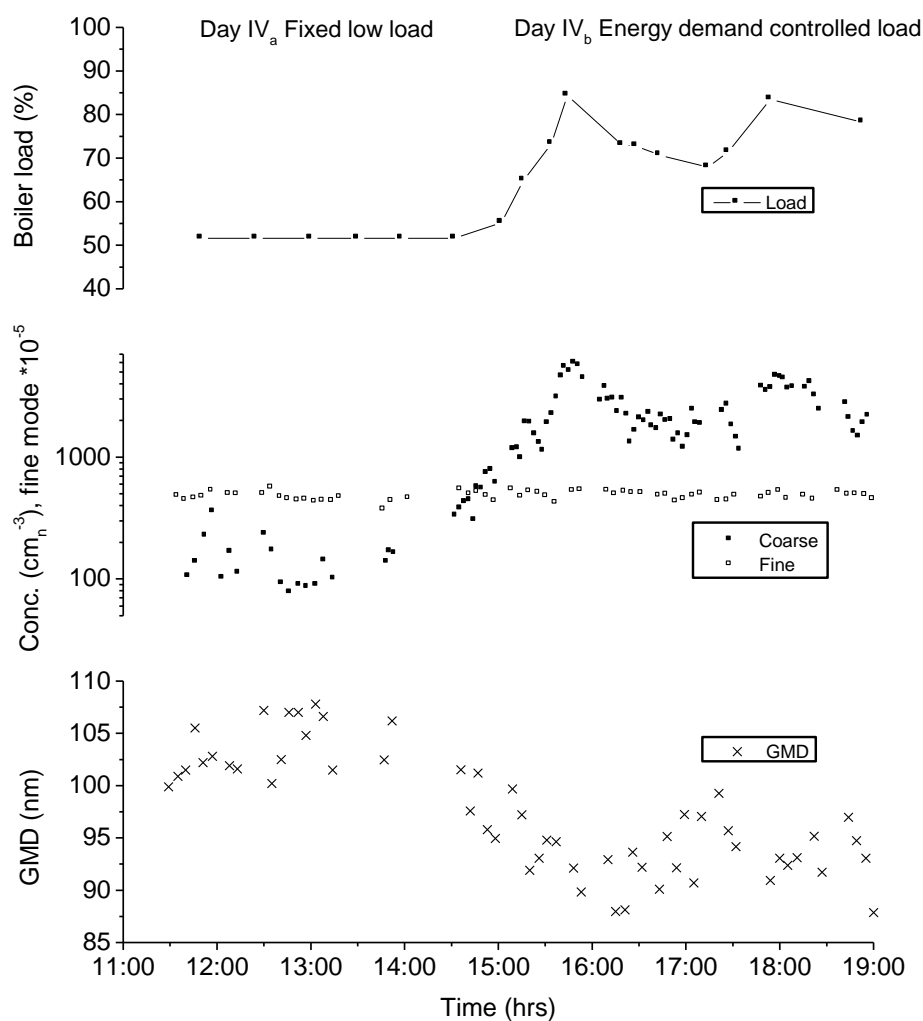
Fig. 4. Boiler load during day IV. Total number of particles > 1 μm and 17-550 nm respectively. Geometric mean diameter of the number distribution of the fine mode particles.
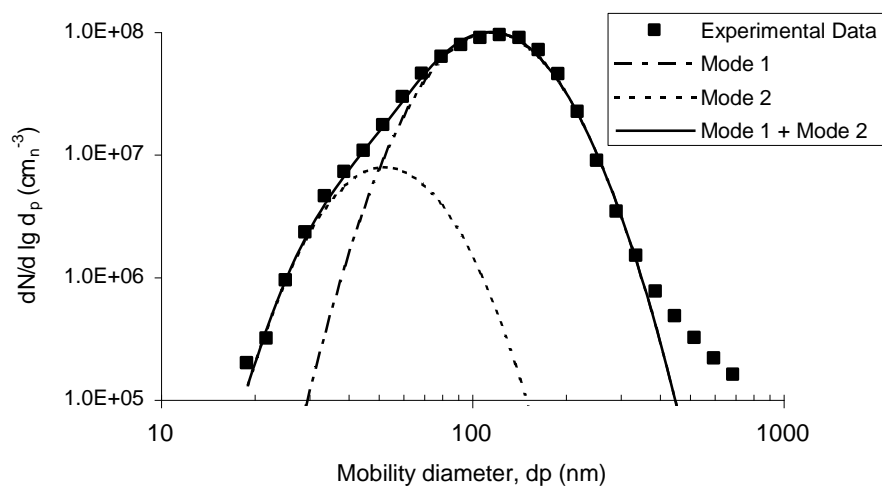

Fig. 5. Average fine mode particle size distribution during day II. Two log-normal modes have been fitted. The experimental data above 400 nm were overestimated due to the relatively long response time of the CPC.
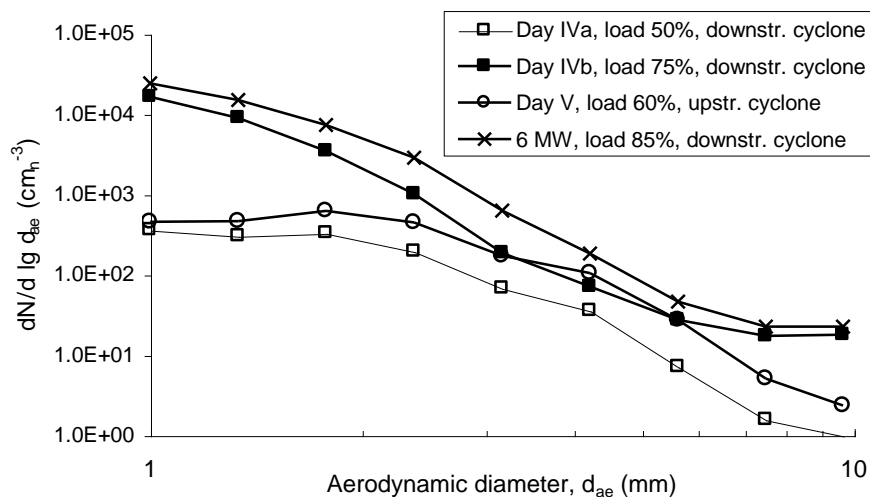
Fig. 6. Coarse particle number size distributions detected by the APS. Data from day IV in the 1 MW and data from the 6 MW boiler sampled downstream the multi-cyclone. Data taken during day V in the 1 MW boiler sampled upstream the multi-cyclone.
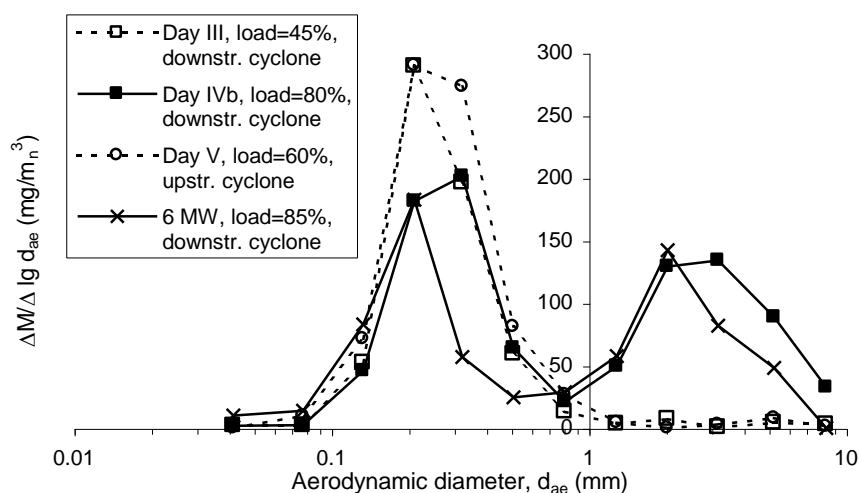
Fig. 7. Particle size distributions according to the gravimetric analysis of the DLPI samples. The gravimetric analysis was performed at RH<30%. The coarse mode data have been corrected for particle loss in the sampling system.
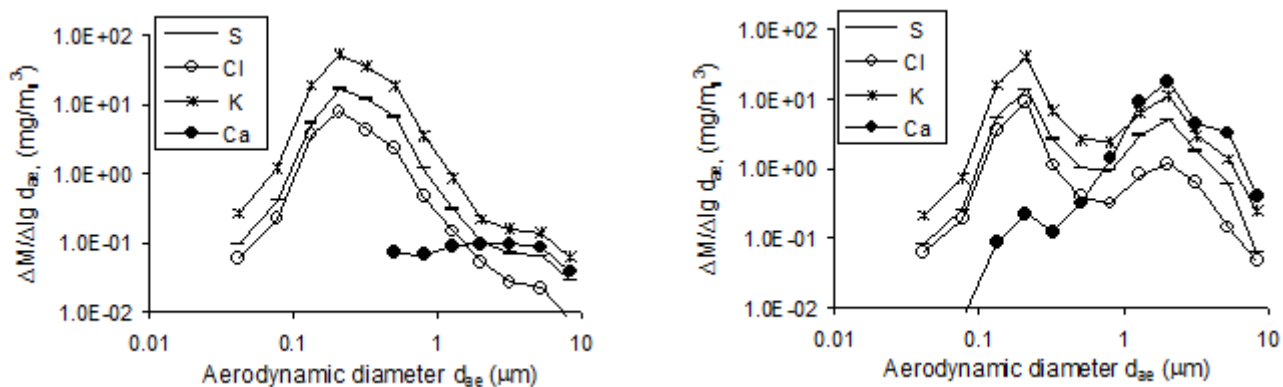

Fig. 8. Particle size distribution of the four major elements as determined by PIXE. The DLPI samples were taken in the 1 MW boiler at 45% load on day III (left) and in the 6 MW boiler at 85% load (right).
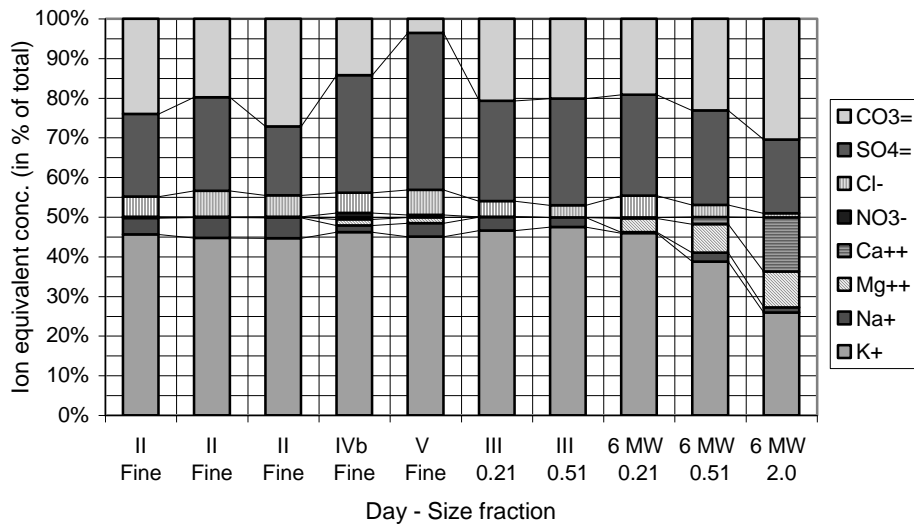
Fig. 9. The results of the ion chromatography analysis of aerosol particles collected in the SFU 2nd stage (first five samples from left) and on selected halves of the impactor substrates (last five samples from left), the mean diameter of the particles in the impactor stage is given in μm. The CO_3^{2-} concentration has been assessed by the assumption that molar balance prevailed and that the contribution of other not detected positive and negative ions was negligible.
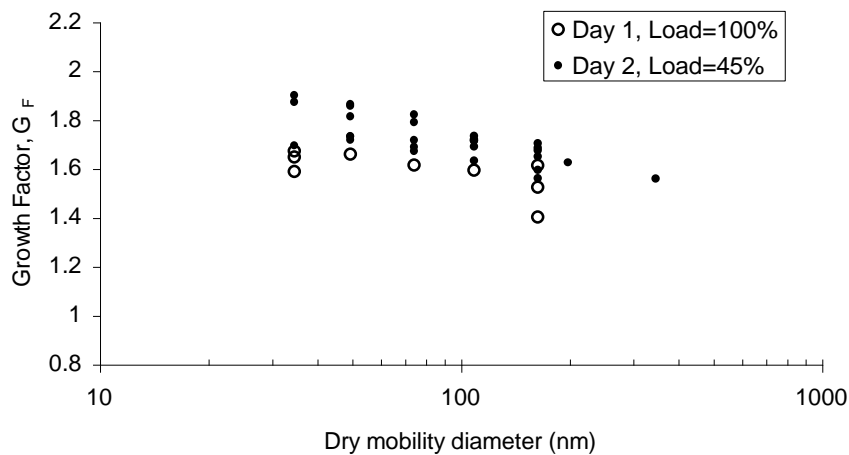

Fig. 10. Particle hygroscopic growth factors defined as the particle diameter at RH=90% divided by the diameter at RH<10%. Results from the 1 MW boiler.
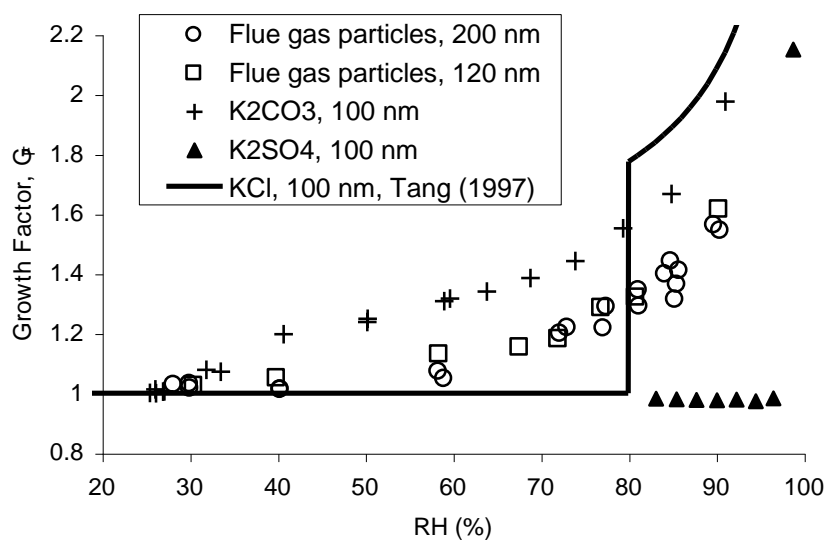
Fig. 11. Results of the deliquescence scans using the H-TDMA. The measurements of flue gas particles were taken in the 1 MW boiler during day II at 45% load. Two separate series were taken at 200 nm and one at 120 nm. The data of pure K_2CO_3 and K_2SO_4 were taken separately in a laboratory. The data of KCl represents modelled values (Tang, 1997).