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**FINE PARTICLE FORMATION AND EMISSIONS IN
BIOMASS COMBUSTION**

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Academic dissertation

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ABSTRACT

Biomass combustion generates large amounts of fine particles that may lead to high flue gas emissions and consequent adverse health effects. The fine particles produce fouling of heat exchangers and may have unpredictable effects in climate. Small scale combustion units are often not equipped with efficient flue gas cleaning units and thus, the fine particle emissions can be high. The fuel choice and combustion technology considerably affect the emissions. Since the thermal utilization of biomasses is likely to increase in the future, these problems may become more severe. The objectives of this work were to characterize fine particles and emissions formed in continuously operated biomass-fired appliances and to assess the role of different factors in fine particle formation.

A set of combustion experiments were carried out in the laboratory and in the field with a number of biomass fuels. The combustion units studied were residential scale boilers, small district heating boilers, a modern pellet stove and a laboratory reactor. Fine particle concentrations, size distributions and chemical compositions as well as gaseous compounds in the flue gas were measured, with several techniques. In addition, the chemical characterization of the fuels and equilibrium calculations were carried out to assess the factors which are important in fine particle formation.

With currently used wood fuels, the amount of fine particles generated were between 13-92 mg/MJ (as PM₁) and $1-5 \times 10^{13}$ particles/MJ. The geometrical mean diameter of the particles varied between 60 and 150 nm. The fine particles were composed mainly of ash material which contained primarily alkali metal salts and zinc. The fractions of soot (elemental carbon) and organic carbon formed due to incomplete combustion were between 0-22 % of the total PM₁. Wood bark material generated clearly higher fine particle emissions than stem materials due to higher fuel ash and potassium contents. The cereal fuels (oat, rape seed, rape seed residue) and peat had fine particle emissions comparable to those of stem wood fuels, despite high fuel ash contents. In contrast to wood fuels, the cereal biomasses produced considerable fractions of phosphate in the fine particles.

In continuously operated biomass-fired appliances the release of alkali metals from the fuel was the main factor in the formation of fine particles. The observed release fractions were highest for stem-rich wood materials and lowest for peat and cereal fuels. Alkali metal release fractions correlated with fuel silicate contents and fuel S/Cl ratios. Furthermore, the release fractions were clearly lower in gasification combustion than in grate combustion technology. The release of zinc was relatively high with all fuels and combustion technologies.

On the small district heating scale, the biomass-fired grate boilers generated clearly higher PM₁ than heavy fuel oil (HFO) boilers, but comparable particle number emissions. The use of electrostatic precipitators in biomass boilers decreased PM₁ by around 95 %, resulting in similar PM₁ as in HFO boilers. However, the PM₁ chemical compositions vary largely between biomass and HFO boilers. Furthermore, biomass fuels and HFO generate different amounts of gaseous SO₂ and NO_x, which participate in the formation of secondary particles in the atmosphere.

The fine particle emissions of biomass combustion can be decreased by flue gas cleaning systems, by modifying the fuel feedstock by different fuel blends or additives, and by developing air staging technology in the combustion units.

Keywords: Aerosols, Air pollutants, Ash, Biomass, Boiler, Burner, Combustion, Combustion aerosols, Emissions, Fine particles, Fuel, Pellets, Small-scale combustion, Smoke, Wood

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Olli Sippula

List of acronyms and definitions

Aerodynamic diameter (d_a)	Diameter of a standard-density (1000 kg/m^3) spherical particle having the same gravitational settling velocity as the observed particle
BLPI	Berner low pressure impactor
Coarse particles	Particles larger than $1 \text{ }\mu\text{m}$ in diameter
CPC	Condensation particle counter
DLPI	Dekati low pressure impactor
DMA	Differential mobility analyser
d_p	Particle diameter
DR	Dilution ratio
EC	Elemental carbon
ELPI	Electrical low pressure impactor
ESP	Electrostatic precipitator
Fine fly ash	Ash material in fine particles
Fine particles	Particles smaller than $1 \text{ }\mu\text{m}$ in diameter
FMPS	Fast mobility particle sizer
FTIR	Fourier transform infra-red analyser
GMD	Geometric mean diameter
ICP-MS	Inductively coupled plasma mass spectrometry
IPCC	Intergovernmental Panel on Climate Change
Mobility diameter	Diameter of a spherical particle with the same dynamic mobility as the observed particle
NTP	Normal temperature and pressure (in this work $20 \text{ }^\circ\text{C}$ and 101325 Pa)
OC	Organic carbon
PAH	Polycyclic aromatic hydrocarbons
PM1	Mass of particles below aerodynamic diameter of $1 \text{ }\mu\text{m}$
PM2.5	Mass of particles below aerodynamic diameter of $2.5 \text{ }\mu\text{m}$
SEM	Scanning electron microscopy
SMPS	Scanning mobility particle sizer
Soot	Fine particles composed of elemental carbon
Stokes diameter	Diameter of a spherical particle with the same density and settling velocity as the observed particle
TSP	Mass of total suspended particles
VOC	Volatile organic compounds

List of publications

This thesis is based on 6 publications referred in the text by their Roman numerals (I-VI). The publications are reproduced with the kind permission of the journals concerned.

- I** Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi, J. (2009) Particle Emissions from Small Wood-Fired District Heating Units. *Energy & Fuels* 23, 2974-2982.
- II** Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi, J. (2009) Comparison of particle emissions from small heavy fuel oil and wood fired boilers. *Atmospheric Environment* 43, 4855-4864.
- III** Sippula, O., Hytönen, K., Tissari, J., Raunemaa, T., Jokiniemi, J. (2007) Effect of Wood Fuel on the Emissions from a Top-Feed Pellet Stove. *Energy & Fuels* 21, 1151-1160.
- IV** Sippula, O., Lind, T., Jokiniemi, J. (2008) Effects of chlorine and sulphur on particle formation in wood combustion performed in a laboratory scale reactor. *Fuel* 87, 2425-2436.
- V** Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J. (2008) Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. *Energy & Fuels* 22, 2033-2042.
- VI** Sippula, O., Hokkinen, J., Lamberg, H., Puustinen, H., Yli-Pirilä, P., Tissari, J., Jokiniemi, J. (2009) Particle emissions from small biomass and fuel oil fired heating units. *17th European Biomass Conference & Exhibition*. Proceedings of the International Conference held in Hamburg, Germany 29 June – 3 July 2009, 1329-1337.

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1 INTRODUCTION

1.1 Background

Attempts to decrease greenhouse gas emissions, and the limited availability of fossil fuels, are increasing interest in using biomasses as fuels for energy production. The EU has set a target to produce at least 20 % of energy with renewable sources by 2020 (for Finland 38 %) (Commission of the European Communities, 2007). A significant proportion of this will be produced by the combustion and co-firing of biomass fuels.

Combustion of biomass fuels generates substantial amounts of fine particles (particles smaller than 1 μm in aerodynamic diameter). If no effective flue gas cleaning systems are in use, most of these particles are released into ambient air, affecting air quality and the climate system. In addition, a fraction of the particles deposit on boiler surfaces, causing operational problems such as reduced efficiency, plugging and corrosion. The characteristics of the aerosol particles formed (particle size, chemical composition and structure) essentially determine their effects on the environment, health and boiler operation.

Particulate air pollution is an important health concern worldwide. Several studies have shown that increased particle concentrations in the ambient air correlate with adverse health effects in the exposed population, including respiratory and cardiovascular illnesses as well as increased mortality (Samet et al., 2000). Further, it has been observed that in the case of combustion-related particles, the fine particle fraction (PM1 or PM2.5) is especially harmful to human health (Schwartz et al., 1996). Thus, road traffic and residential biomass combustion especially have been accused of producing harmful particulate pollutants, since they generate high amounts of fine particles at low emission heights (Karvosenoja and Johansson, 2003, Tiitta et al., 2002, Boman et al., 2003). However, the relationships between largely varying particle physical and chemical properties and the health effects are still not understood. Chemical properties such as the contents of transition metals, polycyclic aromatic hydrocarbons (PAH), organic material, elemental carbon and acidity of the fine particles have been suggested to be the key properties related to the adverse health effects (Lighty et al., 2000, Kennedy, 2007). It has also been suggested that ultra-fine particles (< 100 nm in diameter) might be the most harmful fraction of fine particles due to their high penetration efficiency into alveolar regions of the lungs and further into blood circulation (Lighty et al., 2000). In the case of biomass combustion, PAH- and zinc- containing fine particles have been proposed to cause high toxicity (Fernandez et al., 2001, Durant et al., 1996).

Fine particle emissions from combustion sources directly affect the climate by absorbing and scattering sunlight. Elemental carbon-containing fine particles are known to absorb sunlight, thus contributing to global warming. In contrast, sulphate particles scatter sunlight, and therefore

have a cooling effect (Shindell and Faluvegi, 2009, IPCC, 2007). In addition, fine particle emissions affect the climate indirectly through their influence on cloud formation. These effects are also strongly dependent on the chemical properties of aerosols (IPCC, 2007). Moreover, mixing of various materials in the particles may have unpredictable effects on the climate system. For example, recent findings indicate that the formation of sulphate layers on soot particles increases the warming effect of soot (Moffet and Prather, 2009).

Another concern is the influence of biomass fuel on boiler operation. Aerosol particles and condensable vapours released from the fuel interact with boiler walls, especially with heat exchangers whose surface temperatures are clearly below those of the flue gas. In power-producing boilers, the main problems are usually superheater fouling and corrosion. Costly shutdowns of biomass-firing powerplants due to these problems have been reported (Tobiasen et al., 2007). These disadvantages are usually related to alkali metal-containing aerosols that are responsible for the creation of low-melting point sticky surfaces on the heat exchanger surfaces (Bryers, 1996). The deposition of alkali-containing aerosols can cause melting and sintering of ash deposits, producing tenacious deposit layers that are difficult to remove by soot blowing, and often require manual cleaning (Tobiasen et al., 2007, Bryers, 1996). Moreover, the corrosion rates of superheater tubes have been observed to be clearly related to the chlorine in the deposits, transferred mainly as alkali chlorides (Van Loo and Koppejan, 2008, Michelsen et al., 1998). In addition to alkali metals, other volatile condensable ash species, for example zinc, have also been observed to be harmful to heat exchangers (Backman et al., 2005, Bankiewicz et al., 2009).

1.2 Motivation

The increasing use of bioenergy requires new biomass sources for combustion processes. Many of these fuels have high ash contents and varying ash compositions, including problematic elements such as potassium, chlorine and zinc. This may lead to high emissions, especially fine particle emissions, as well as operational problems. In addition, the usability of fuels varies among different combustion appliances. Understanding the dependency between fuel composition and particle and emission formation is essential when new fuel materials are considered for use. First, this helps in finding optimal fuels and fuel mixtures to minimize harmful particle formation and flue gas emissions. Secondly, the information is needed to predict emission formation in the designing of the energy production units to meet the emission regulations and to assess the environmental effects of different alternatives.

At the time this study began, there was a clear lack of knowledge of the effects of biomass fuel material on fine particles formed during combustion. First, data regarding the release behavior of ash-forming elements in real-world combustion units was very limited. Second, the chemical and physical properties of fine particles formed in combustion of alternative biomasses,

such as crops and wood bark, were still poorly known. In addition, there was a lack of information on fine particle emission factors and characteristics of fine particles in residential combustion appliances and in small-scale district heating boilers.

1.3 Objectives of this thesis

The aims of this study were to characterize fine particles formed in continuously operated biomass-fired appliances, and to assess the role of different factors in the processes that lead to their formation. The main considerations were the fuel raw material and the composition of ash-forming materials in the fuels. In addition, experiments with various boiler types were performed.

The detailed objectives were:

- To characterize aerosol particles formed in small heating boilers fired with biomass (**Paper I, Paper VI**).
- To determine the effect of fuel raw materials on fine particle formation and emissions (**Paper III, Paper V, Paper VI**).
- To find out the effects of fuel ash composition on fine particle formation and emissions (**Paper IV, Paper V, Paper VI**).
- To describe fine fly ash formation mechanisms in biomass-fired appliances (**Paper II, Paper III, Paper IV**).
- To compare fine particle emissions from biomass and from heavy fuel oil combustion (**Paper II, Paper VI**).

2 SCIENTIFIC BACKGROUND

2.1 Combustion technologies

Several techniques exist for the combustion of solid fuels. These can be divided into:

- fixed bed combustion
- fluidized bed combustion
- pulverized fuel combustion

In fixed bed combustion the primary combustion air is supplied through a bed of fuel, where drying, gasification and char combustion take place. In most of the combustion systems the air supply is divided into two or more locations. In these systems the combustible gases released from the fuel bed are burned with secondary air additions that are often located separately from the primary combustion zone (Van Loo and Koppejan, 2008). Fixed bed combustion systems are flexible regarding moisture content and fuel particle size (Obernberger, 2009). Typical fixed bed combustion systems are grate furnaces and under-feed stokers. Most small-scale combustion appliances are fixed bed systems. In grate combustion systems, there are several different grate designs, including fixed grates, travelling grates, rotating grates and vibrating grates. These all have specific advantages and disadvantages depending on fuel properties (Yin et al., 2008).

In fluidized bed combustion, fuel is burned in a suspension of gas and solid bed material (usually sand). The primary air enters from below the bed. Two different technologies, bubbling fluidized bed combustion (BFB) and circulating fluidized bed combustion (CFB), can be distinguished. In BFB, the fluidization velocity is lower and the bed material is located in the bottom part of the furnace. In CFB, the fluidization velocity is high and thus the bed particles are carried with the flue gas, separated in a cyclone and circulated back into the combustion chamber (Van Loo and Koppejan, 2008). Fluidized bed systems are generally flexible regarding fuel materials and moisture but inflexible regarding fuel particle sizes (Obernberger, 2009).

In pulverized fuel combustion, a mixture of primary combustion air and pulverized fuel is injected into the furnace. The combustible gas burnout is achieved after secondary air addition. The technology requires small fuel particle sizes and low moisture contents (Van Loo and Koppejan, 2008, Obernberger, 2009).

2.2 Biomass fuel

Biomass fuels are biological materials derived from various living organisms. The most common sources of biomass fuels are trees (e.g. forest residues) and cultivated plants (e.g. straw).

Although the characteristics of biomass fuels vary largely, in general there are some common properties which make them considerably different from fossil solid fuels. These differences also play an important role in regard to aerosol formation during combustion. First, biomass fuels have generally high volatile material content and low char content, when compared with coal (Van Loo and Koppejan, 2008). (This can be observed as a larger flame than in coal burning). Second, the heating values of the biomass fuels range from 14 to 28 MJ/kg and are generally significantly lower than in fossil fuels (for example, hard coal has a heating value of around 30 MJ/kg, and wood fuels typically around 20 MJ/kg) (Phyllis database for biomass and waste, 2009). Hence, biomass combustion temperatures are usually remarkably below those of fossil fuel combustion. Third, biomass ashes contain high amounts of volatile material, especially potassium, of which a large fraction volatilizes during combustion and forms fine particles (Valmari, 2000).

Biomass ash characteristics. Solid fuels always contain inorganic constituents that form ash during combustion. Some of these ash-forming species volatilize to form the fine fly ash fraction, while the unvolatilised species typically form large ash particles that remain in the bottom of the furnace (bottom ash) or form the coarse fly ash fraction. The ash-forming species are found in solid fuels as included and excluded minerals, salts and ash-forming species bound to organic molecules (Zevenhoven-Onderwater, 2001). The older fuels (e.g. coal) contain mainly minerals, while in biomass fuels a large fraction of the ash-forming material is present in free ionic form, precipitated salts and organic molecules (Van Loo and Koppejan, 2008, Zevenhoven-Onderwater, 2001). Untreated wood material has typically low ash contents. Finnish bark-free wood materials have ash contents usually below 1 % of dry material. However, bark and foliage fractions have clearly higher ash contents, up to 8 % (Werkelin et al., 2005, Alakangas, 2000, **Paper III, Table 2**). The main ash-forming species in Finnish and Scandinavian wood fuels are typically K, Ca, Mg, P, Cl, S, Si, Fe, Mn, Na and Al (Werkelin et al., 2005, **Paper III, Table 2**), of which most are nutrients and essential for plant growth. The clean biomasses typically contain higher amounts of elements forming positive ions (cations, e.g. K, Ca) than elements forming negative ions (anions, e.g. S, Cl and P) (Knudsen et al., 2004a).

Potassium, which is one of the main fine fly ash-forming elements, is present mainly in water soluble form (Van Loo and Koppejan, 2008). Its uptake in the plant is highly selective and correlates with the metabolic activity (Bryers, 1996). Chlorine appears as chloride ion and its concentration is closely related to that of soil (Bryers, 1996, Van Loo and Koppejan, 2008). Sulphur occurs in the form of both ionic sulphate and organic sulphur. Calcium occurs mainly as precipitated minerals and to a small extent in organic macromolecules (Van Loo and Koppejan, 2008). Silicon occurs naturally, mainly precipitated as hydrated oxide (Bryers, 1996) but significant amounts may be present as contamination from the soil (Öhman et al., 2004).

Generally a larger fraction of ash is present in organic molecules in woody biomasses than in field biomasses. Drying of the biomass leads to precipitation of ions in aqueous solution, affecting ash behavior during combustion (van Lith et al., 2008). The water soluble and organically bound (acetate soluble) fractions of the fuel ash have been assumed to be released more easily and be more reactive during combustion than the non-soluble mineral fractions (Pettersson et al., 2008, Frandsen et al., 2007).

2.3 Release of ash

The behaviour of ash-forming species is considerably influenced by the fuel ash properties, i. e. ash composition, the chemical form and binding of the ash-forming materials. In addition, ash behaviour varies largely between different combustion technologies and combustion conditions. The literature concerning properties and behaviour of ashes is vast.

In this thesis, the release of ash means that an ash-forming element vaporizes and “escapes” the fuel particle. These species end up forming either gaseous species (e.g. HCl, SO₂) or fine particles (e.g. KCl, K₂SO₄). In contrast, retention means that the ash species remains in the bottom ash or ends up in the coarse fly ash fraction.

Several factors are known to influence the release and retention of ash species during combustion. First of all, the combustion temperature is generally known to be in clear correlation with the release fractions (Knudsen et al., 2004a, Flagan and Seinfeld, 1988), as can be expected. Second, in coal combustion the release of ash has been found to be affected significantly by the oxidizing/reducing conditions. The reducing conditions increase ash release since the reduced forms of many ash species have higher vapour pressures (Senior and Flagan, 1982). A similar mechanism is likely to affect some ash species in biomass combustion, for example zinc (Elled et al., 2008, Obernberger et al., 2001). Third, the fuel composition affects the release via complex chemical and physical mechanisms. These are still not well enough understood to make accurate quantitative predictions on ash behavior, for example when new fuels are introduced. However, for biomass fuels several composition-dependent relations have been identified (van Lith et al., 2008, Novakovic et al., 2009). In addition, fuel moisture content has been observed to affect ash release (Novakovic et al., 2009). Fourth, the fuel particle and structure and temperature-residence time history affect the measured release rates since the equilibrium of evaporating species may be slow to reach, and on the other hand some volatile species are trapped in the pores of the fuel by physisorption (Knudsen et al., 2004a, Flagan and Seinfeld, 1988).

Release of alkali metals in biomass combustion. The most abundant compounds in the PM₁ of biomass combustion are alkali metals, typically present as sulphates, chlorides, carbonates, hydroxides and sometimes as phosphates. This is because alkali metals are released to a significantly larger extent than other main ash-forming cation elements in the biomass fuels

(Ca, Mg, Al, Fe, Si, Mn). Hence, of major interest in the fine ash particle formation in biomass combustion processes has been the release of alkali metals from the fuel.

Several studies on alkali metal release in different biomasses have been carried out in controlled laboratory conditions. The main findings are that in the devolatilisation stage with low temperatures (< 500 °C) only organically bound alkali metals are released, while the major fraction of alkali release occurs at temperatures above 600 °C and usually mainly in the char burning phase (Valmari, 2000, Olsson et al., 1997, Davidsson et al., 2002, Dayton et al., 1995, Wornat et al., 1995). The release during the low temperature devolatilisation stage is not significantly influenced by fuel composition (e.g. fuel chlorine content), in contrast to the release in the char burning stage (Olsson et al., 1997). Further, van Lith et al. (2008) observed that the released fraction of potassium during pyrolysis of different wood samples was significantly smaller than the organically bound fraction of potassium, which was suggested to be due to the formation of K-char bonds and later K_2CO_3 . In the char burning stage, the alkali release has been shown to be affected considerably by the ash composition and moisture (Knudsen et al., 2004a). Literature on the quantification of alkali release from the fuel into fine particle fraction in real combustion units is very scarce. The observed K and Na release fractions of biomass fuels vary largely, in the range between 1 % and 60 % of the total amount (Wiinikka et al., 2007, Brunner, 2006).

Fuel chlorine has been found to increase alkali release by forming alkali chlorides (Glazer et al., 2005, Baxter et al., 1998), which volatilize at relatively low temperatures, in a temperature range of 700-830 °C according to Jensen et al. (2000b) and Knudsen et al. (2004a). However, the behavior of chlorine is strongly affected by fuel sulphur content. With sulphur rich fuels, alkali sulphates are likely to be formed and consequently chlorine forms HCl gas. This has been observed as lower alkali metal release into the fine particle fraction (Lind et al., 2006). This effect may also be influenced by the formation of mixed sulphates with alkali earth metals (Lind et al., 2006). Sulphur is also likely to decrease the release of other volatile alkali species, such as alkali hydroxides, and possibly some other metals that form sulphates (Miller et al., 2003).

There is only limited data on the effect of fuel moisture on the behavior of alkali metals. An increase in the moisture content has been found to enhance the formation of KOH vapour in straw combustion (Dayton et al., 1995) and increase the release of alkali metals from ashes with various compositions (Novakovic et al., 2009). Knudsen et al. (2004a) hypothesized that the formation of KOH might be due to enhanced decomposition of K_2CO_3 in the presence of water vapour.

Important factors affecting alkali release are fuel silicate and aluminium contents. There are several studies on the formation of alkali silicates, which are stable and non-volatile in combustion conditions, and hinder the release of alkali metals (Glazer et al., 2005, Wei et al., 2002, Dayton et al., 1999). Aluminium silicates (e.g. kaolin) have been reported to effectively

capture alkali metals by a chemical reaction (chemisorption), forming alkali aluminium silicates (Tran et al., 2005, Aho, 2001). As an example, Equations 1-3 present the potassium capture reaction of meta-kaolinite, as suggested by Tran et al. (2005). For other silicates and alumina (Al₂O₃) both chemisorption and physical adsorption have been proposed as the capture mechanism (Shadman and Punjak, 1988, Uberoi and Shadman, 1991, Coda et al., 2001, Dou et al., 2003). X-ray diffraction analyses from bottom ashes of various biomass fuels have revealed the existence of several alkalisilicate compounds (Gilbe et al., 2008, Lindström et al., 2008). There is evidence that the presence of fuel alkali earth metals significantly decreases the retention of alkali metals in the silicate structure by the competition for the ionic positions in silica molecules, indicating the importance of a ternary system including alkali metal, alkali earth metal and silicate for the behavior of alkali metals. (van Lith et al., 2008, Novakovic et al., 2009, Risnes et al., 2003).

In biomass fuels rich in phosphorus, an important system for alkali retention might be the formation of alkali metal–alkali earth metal–phosphate compounds (Novakovic et al., 2009, Sandström, 2006). These compounds are non-volatile and thus their formation decreases the release of alkali metals. They are formed in large quantity when cereal crops and sewage sludge are burned, for example (Sandström, 2006). In addition, phosphate based additives have been utilized successfully to prevent release of alkali metals in straw combustion (Tobiasen et al., 2007)

Practical applications. In Finland co-firing of peat with wood is common because of its positive effect on problems related to alkali metals. It has been proposed that this effect is due to the increased formation of alkali silicate compounds, and the consequent decrease in the alkali release (Lundholm et al., 2005, **Paper VI**). In addition, the relatively high amounts of sulphur in peat may decrease alkali metal release, and on the other hand enhance the formation of alkali sulphates in flue gas, which generate less fouling than alkali chlorides. Similar effects have also been found for many coal fuels (Glazer et al., 2005, Aho and Ferrer, 2005). Thirdly, various additives are used either to decrease alkali metal formation or convert the released alkali metal compounds into less harmful form. These additives have been based mainly on silicates, phosphates and sulphur (Tobiasen et al., 2007, Henderson et al., 2006).



2.4 Formation of combustion aerosol

Combustion aerosol is a dynamic mixture of gases, vapours and particles in a flue gas. According to a common definition of aerosol particles, the particle sizes vary between 1 nm and 100 μm in diameter. The upper boundary is approximately the size of particles which remain airborne long enough to be observed and measured as aerosols. There are different definitions of aerosol particle sizes. They originate from the need to classify particles of different shapes and are often based on different measurement principles. In this thesis, two different particle sizes are referred to. The mobility diameter is equal to the diameter of a sphere with the same mobility as the particle in question. The aerodynamic diameter is the diameter of a standard-density (1000 kg/m^3) sphere that has the same gravitational settling velocity as the observed particle (Baron and Willeke, 2001).

Combustion processes of solid and liquid fuels typically generate aerosol particles that contain two or more distinct particle size modes. These modes usually differ significantly in chemical and physical properties. Particles larger than 1 μm in diameter are often called coarse particles and these particles are typically formed from char or ash residues of the fuel (Flagan and Seinfeld, 1988). In addition, shedding of the deposits from the boiler surfaces may produce coarse particles. In fluidized bed combustion, the attrition of bed sand may be an important mechanism in the formation of coarse particles (Lind, 1999). The fine particle modes are generally formed from species that have vaporized during combustion, which later saturate and form fine particles by nucleation. The nucleated particles grow further by coagulation and agglomeration, condensation and surface reactions. All these particles are called primary particles. In addition, some gases and vapours released in the combustion process may form aerosol particles in the diluting exhaust plume or later in the atmosphere. These particles are called secondary aerosol particles. The secondary particles may sometimes be seen in the measurements as a third mode consisting of ultra-fine particles ($d_p < 100 \text{ nm}$) (Kittelson, 1998), and are sometimes called secondary nucleation mode. This thesis focuses mainly on the primary particles formed in the combustion process.

Generally speaking, primary fine particles can be divided to three categories according to their origin and formation mechanisms: ash (inorganic), soot (elemental carbon) and organic material (e.g. Lighty et al., 2000). Ash originates from non-combustible material introduced into the furnace, while soot and organics are combustible material. The formation of different type of primary particles are reviewed in chapters 2.4.2, 2.4.3 and 2.4.4.

2.4.1 Particle formation and transformation mechanisms

The nucleation of particles is a result of vapour-molecule collisions which form molecular clusters. Some of the clusters may grow to a critical size that, as a result of further molecular collisions, grow faster than they disassociate, and form stable aerosol particles. The critical saturation ratio required for the formation of stable clusters varies considerably and depends on the vapour phase substances, prevailing physical conditions and the existence of foreign materials. In the case of homogeneous nucleation, the particles are formed of one or several substances which are all initially in the vapour form, while in heterogeneous nucleation foreign materials assist in the formation of stable clusters (Kulmala et al., 2000, Seinfeld and Pandis, 2006). In flue gases, the saturation of the fine particle-forming vapours may occur because of temperature decrease, or by oxidation of the vapour, for example when the species enter from the reduced combustion zone into oxygen rich zone, or by other chemical reactions which lead to the formation of low vapour pressure species (Flagan and Seinfeld, 1988, Jokiniemi et al., 1994).

The growth mechanisms of aerosol particles involve vapour condensation, coagulation, agglomeration, surface reactions and adsorption. The growth of particles by condensation depends on the particle size and saturation ratio. In general, smaller saturation ratios are required for condensation than for homogeneous nucleation of particles. Thus, the cooling rate, mixing and chemical reactions of the condensable species are important in the nucleation-condensation dynamics of combustion systems (Jokiniemi et al., 1994, Christensen et al., 1998).

Particle growth by coagulation and agglomeration results from collisions of aerosol particles with each other. In general, when submicron particles collide, they stick together. Collisions may be caused by Brownian motion (thermal coagulation) or by external forces (kinematic coagulation) (Hinds, 1999). Particle size, chemical composition and process conditions determine the properties of these particles. If the colliding particles are liquid, they coalesce and form new spherical liquid droplets. At the other extreme, the colliding particles are solid and stay together by Van der Waals attraction. In this case, dendritic structures are formed and the process is called agglomeration (Lehtinen, 1997). In reality, agglomerates formed in combustion processes tend to coalesce partly and may restructure, forming particles with a complex morphology (Lighty et al., 2000, Flagan and Seinfeld, 1988).

2.4.2 Formation of soot

Soot particles are formed already inside the flame in the fuel-rich area via complex mechanisms, involving the formation of soot nuclei from gaseous hydrocarbons and particle growth by surface reactions, coagulation and agglomeration (Bockhorn, 1994). For biomass combustion, there is a very limited literature available concerning soot formation. The formation

process depends largely on the fuel and flame type. On a general level, two pathways for the formation of soot nuclei have been proposed. First, at lower temperatures aromatic hydrocarbons produce soot directly by growing into graphite-like structure. Second, at higher temperatures both aliphatic and aromatic hydrocarbons first fragment, which is followed by polymerization of the fragments to larger molecules, forming soot (Amann and Siegl, 1981). In wood combustion, the decomposition products of lignin have been suggested to play an important role in the soot formation (Fitzpatrick et al., 2007, Fitzpatrick et al., 2008, Baeza-Romero et al., 2010). Soot formation and structure are described in more details in Haynes and Wagner (1981), Flagan and Seinfeld (1988), Bockhorn (1994), Ishiguro et al. (1997), Fitzpatrick et al. (2008) and Glarborg (2007). Soot burn out occurs mainly in the flame, and the conditions in the oxygen-rich zone at the end of the flame have been found to be desirable for soot burn out (Tree and Svensson, 2007, Wiinikka et al., 2006). In industrial-scale biomass combustion units, the amounts of soot in the emissions are typically negligible (**Paper I**), while in traditional small-scale combustion units, soot is an important fraction in fine particle emissions (Tissari et al., 2008).

2.4.3 Formation of fine fly ash

Fine ash particles are generally formed from volatilized ash species which condense either when the temperature decreases or when chemical reactions form lower vapour pressure species. In recent decades, inorganic fly ash particle formation has been extensively studied in connection with pulverized coal combustion.

Pulverized coal combustion. In combustion of high-rank coals, fine particles are formed mainly from different refractory species (Si, Ca, Mg, Fe, Al). For pulverized coal combustion, mechanistic mathematical models for the formation of these particles have been developed (Flagan and Seinfeld, 1988, Senior and Flagan, 1982). The formation starts with the reduction of the ash species to suboxides or into elemental form and the consequent vaporization from the fuel particle. These reduced species oxidize in the boundary layer of a fuel particle, causing a rapid supersaturation, and form very small particles by homogeneous nucleation. The resulting fine particle size distribution is determined mainly by collisions of these boundary layer-generated particles (Flagan and Seinfeld, 1988, Senior and Flagan, 1982).

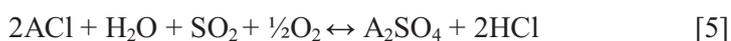
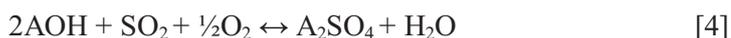
Seed particles in biomass combustion. A similar mechanism as for pulverized coal combustion for boundary layer generated seed particle formation might also exist with biomass fuels. One remarkable difference in biomass combustion is the high content of alkali metal vapours (K and Na) that condense and enrich in the fine particle fraction in cooling flue gas at lower temperatures than refractory species (Christensen et al., 1998, Valmari et al., 1998). The question whether alkali metal condensation occurs on seed particles or starts with nucleation is currently not yet answered.

In biomass combustion, probable seed forming species are volatile metals that in an oxidizing environment form compounds with low vapour pressures. Zn, Pb, Ni, Cd, Cu, As and Tl especially have a tendency to release in fine particle fraction, though the release behaviour is strongly dependent on the fuel composition and combustion technology (Oberberger et al., 2001, Lind et al., 2003, Lind et al., 2000, Lundholm et al., 2007, Jiménez et al., 2008). Many of these species may condense above 900 °C (Jiménez et al., 2008) and therefore act as seed particles in alkali compound condensation. The trace species have special importance in the co-firing of wastes (Lind et al., 2003) or the combustion of waste wood (Oberberger et al., 2001). However, clean wood fuels also contain significant amounts of zinc, which has been found to enrich in high fractions in fine particles (Wiinikka et al., 2007, Wiinikka et al., 2006). Zinc is likely to be vaporized as elemental zinc vapour, which has a relatively high vapour pressure, while oxidation of zinc to ZnO causes a steep decrease in vapour pressure and probably nucleation in biomass combustion environments (Weidenkaff et al., 1999, Jöller et al., 2007). The gas-to-particle conversion of zinc is likely to begin before that of alkali metals, and Jöller (2007) concluded that in grate combustion of wood fuels, ZnO particles are formed already in the primary zone of the furnace above the fuel bed. However, with chlorine-rich fuels, formation of ZnCl₂ is favoured (Elled et al., 2008), which delays the condensation until low temperatures are reached (< 300 °C) (Jöller et al., 2005). ZnO particles may act as condensation seeds for alkali sulphates, and suppress their nucleation, depending on the surface area of the seed particle population and flue gas cooling rate (Jöller et al., 2007).

Alkali metals in biomass combustion. According to current understanding, the alkali metal vapours are released from the biomass fuel particle mainly as chloride vapours (KCl, NaCl) and hydroxide vapours (KOH, NaOH) (Dayton et al., 1995, Baxter et al., 1998, van Lith et al., 2006). However, these species usually transmute in the flue gas through reactions with other gaseous species. From a pure wood fuel with clean combustion conditions, the emitted fine fly ash fraction is typically formed of alkali sulphates, chlorides and carbonates (Valmari et al., 1998). In addition, alkali hydroxides, phosphates, nitrates and K₃Na(SO₄)₂ have been observed or are theoretically possible products (Wiinikka et al., 2007, Christensen et al., 1998, Valmari et al., 1998, Mikkanen et al., 1999, Jiménez and Ballester, 2005). With phosphorus-rich fuels, alkali phosphates have been found to be one of the major compounds in the fine particle emissions (Christensen et al., 1998, Bäfver et al., 2009). The experimentally observed fine particle compositions are often consistent with the calculated thermodynamic equilibrium compositions in the flue gas (Wiinikka et al., 2006). However, at least alkali sulphate and carbonate formation have been reported to be limited by reaction kinetics (Christensen et al., 1998, Valmari et al., 1998)

Since the gas-to-particle conversion of alkali metals in typical flue gas conditions begins via the sulphation of alkali metals, this reaction is of particular importance for the formation of

fine particles. The global reactions for sulphation of alkali chlorides and hydroxides are shown in Equations 4 & 5. These reactions become thermodynamically favoured typically below certain flue gas temperatures, ranging from 1000 to 1200 °C (Baxter et al., 1998). The formation of alkali sulphates leads to saturation, and either nucleation of the species to form new particles or condensation on existing fine seed particles (Jokiniemi et al., 1994). Laboratory studies indicate that these reactions take place mainly in the gas-phase (Iisa et al., 1999, Jensen et al., 2000a), although there are contrary opinions, claiming heterogeneous sulphation process (Steinberg and Schofield, 1990, Steinberg and Schofield, 2002). Christensen et al. (1998) suggested that in a straw-fired industrial-scale boiler the reaction follows equilibrium down to a temperature of about 850 °C, while at lower temperatures the kinetics slow down the reactions, and at 750 °C no sulphation occurs, although it is thermodynamically favoured. The rate limiting step for the sulphation reaction has been suggested to be the oxidation of SO₂ to SO₃• (Glarborg and Marshall, 2005), and more recently the oxidation of sulphite to sulphate (Hindiyarti et al., 2008). According to Hindiyarti et al. (2008), no SO₃ as an intermediate product, is necessary for the sulphation reaction. Christensen and Livbjerg (1996, 2000) and Pyykönen et al. (2005) have performed simulations on alkali aerosol formation in biomass combustion processes. The simulations indicate that the nucleation-condensation dynamics of alkali sulphates can determine the formation of fine particles and the produced particle number while the role of coagulation still remains unclear. The gas-to-particle conversion of alkali sulphates is followed by the condensation of alkali chlorides and, if the flue gas contains more alkali metals than can be bound to S and Cl, by the formation of alkali carbonates from alkali hydroxides at lower temperatures. Since the sulphation and carbonation reactions can be kinetically limited, some alkali hydroxide vapours may also condense or they may form other compounds, such as nitrates (Christensen et al., 1998, Christensen and Livbjerg, 1996).



Where A = K or Na.

2.4.4 Formation of particulate organic material

When biomass is heated, it decomposes forming a large variety of different organic compounds, with highly different vapour pressures and molecular structures (Rogge, 2003, McDonald et al., 2000). Organic compounds can remain in the flue gas due to incomplete combustion. According to Simoneit et al. (1999), the major particulate organic components in biomass combustion are

monosaccharide derivatives (e.g. levoglucosan), from the breakdown of cellulose, and lesser amounts of aliphatic and oxygenated compounds, terpenoids, resins, gums and other biopolymers. The main part of the organic material found in fine particles is usually condensed at significantly lower temperatures than inorganic species, and considerable amounts may condense first during the dilution of the smoke (Lipsky and Robinson, 2006). In flue gas conditions, the organic vapours condense mainly on existing fine particles via condensation and/or adsorption (Tissari et al., 2008). However, in the exhaust plume, dilution with rapid cooling may produce homogeneous nucleation of semivolatile organic vapours, observed as separate nucleation mode in the particle size distribution (Pyykönen et al., 2007, Lipsky and Robinson, 2005).

2.4.5 Formation of coarse particles

The coarse particles ($d_p > 1 \mu\text{m}$) in solid fuel combustion processes are generally formed of non-volatilised ash, and sometimes of unburned fuel, which are entrained into the flue gas. Burning of a fuel particle leaves ash residues that may subsequently agglomerate and fuse together or break up into smaller pieces. (Flagan and Seinfeld, 1988). Furthermore, in fluidized bed combustion, a significant amount of coarse ash particles are formed by attrition of the bed sand (Lind, 1999). In industrial-scale biomass combustion, the coarse particle fractions have been observed to consist of non-volatile compounds such as alkali earth metals (Ca, Mg), sulphates, oxides, phosphates and silicates (Valmari et al., 1998, Brunner, 2006). However, coarse fly ash fraction may also contain significant amounts of volatile ash species such as alkali metals. An aerosol dynamics modeling study in large-scale biomass boiler conditions (Jokiniemi et al., 2001) showed that the condensation of ash-forming vapours is not likely to occur on the surfaces of coarse ash particles, and the presence of volatile species in coarse ashes indicate non-complete vaporization, surface reactions and/or re-entrainment of deposited material from the boiler walls.

2.5 Aerosol deposition in flue gas passage

In combustion systems some of the released vapours, fine particles and coarse particles interact with walls, which leads to deposition. In boilers, the mechanisms for the deposition of fine particles are boundary layer thermophoresis caused by the temperature gradient between the flue gas and boiler walls, and Brownian diffusion. Thermophoresis plays an important role in heat exchangers, while Brownian diffusion is an important mechanism only for ultra-fine particles relatively independent of the temperature conditions (Eskola et al., 1998). In addition, in power-producing boilers, condensation of alkali metal vapour on superheater tubes is an important deposition mechanism (Pyykönen and Jokiniemi, 2003). There is very limited information on the fraction of fine particle deposition in practical combustion systems. A modeling study of fine

particle deposition in a fluidized bed watertube boiler for combined heat and power production, gave an estimation of fine particle deposition rate of 5 % (including vapour deposition) (Jokiniemi and Sippula, 2009).

For coarse particles, the deposition mechanisms are based on thermophoresis (for $d_p < 10 \mu\text{m}$) and inertial forces, which involve inertial impaction and turbulent eddy impaction (Eskola et al., 1998). The deposition rates are typically high in areas with bends or obstacles, but on the other hand there is constant shedding and resuspension of the deposit material in the flue gas flow (Zbogor et al., 2009).

2.6 Fine particle emissions

The levels of particle emissions and their chemical and physical characteristics are strongly dependent on fuel properties, combustion conditions and flue gas cleaning technology. Small-scale biomass combustion is generally an important source of ambient fine particles due to the lack of flue gas cleaning systems. In addition, biomass combustion processes may generate nitrogen oxides (NO_x), sulphur dioxide (SO₂) and volatile organic compounds (VOC) that participate in the secondary particle formation in the atmosphere (IPCC, 2001).

In small-scale energy production, combustion technologies and fuels vary largely. Information on fine particle emissions from this sector is still relatively scarce and restricted to a few boiler and stove types, and the most common fuels.

The highest emissions in relation to energy produced are usually generated in residential-scale combustion (< 100 kW). The fine particles may contain high amounts of soot and organic material, especially in appliances that are operated batch-wise and with natural draught. In these appliances, the nominal PM₁ emissions range typically between 35 and 250 mg/MJ (Tissari et al., 2009).

The continuously fired small-scale applications allow more optimized combustion conditions, and lower emissions. The diversity in this type of combustion technologies is also high, and thus emission factors vary considerably. With constant operation, total particle emissions from 12 to 89 mg/MJ have been measured (Johansson et al., 2004), which is estimated to consist mainly of fine particles (Bäfver, 2008). Typical PM₁ emissions for a modern pellet boiler system have been found to vary from 5 to 25 mg/MJ, depending on the operation of the boiler (Lamberg et al., 2009).

In larger appliances, such as district heating facilities and power plants, the fine particle emissions are generally composed entirely of ash material. These boilers usually have flue gas cleaning technology, and thus the particle emissions are strongly affected by the particle filtration efficiency (Ohlström et al., 2000, **Paper I**). Many small district heating plants are still in operation without effective particle removal systems. Their nominal fine particle emissions are

on a similar level with those of modern residential-scale appliances, though the chemical composition is different (Pagels et al., 2003, Wierzbicka et al., 2005).

The most common particle separation techniques include cyclones, electrostatic precipitators (ESP), baghouse filters and scrubbers. The cyclones remove only coarse particles, while the other technologies can be used for removing both fine and coarse particle fractions (Ohlström et al., 2000, **Paper I**). For effective fine particle filtration, the most common filters are ESPs and baghouse filters.

3 METHODS

The work included experiments in the laboratory and in the field, applying measurements and analyses on the physical and chemical properties of the aerosol particles. In addition, measurements of flue gas compositions, chemical characterizations of the fuels and thermodynamic equilibrium modeling were carried out to assess fine particle formation mechanisms.

3.1 Combustion experiments and aerosol sampling systems

The biomass combustion experiments in this thesis were carried out in the field at 5 different boilers, in the laboratory with 2 different pellet combustion appliances and with a laboratory-scale laminar flow reactor. All experiments focused on characterizing the chemical and physical properties of the combustion aerosols. The fuels were mainly different Finnish wood materials but included also peat (**Papers V & VI**) and cereal fuels (**Paper V**). In addition, fuel ash compositions were modified by additives (**Papers IV & V**). The combustion appliances are listed in Table 1. The main fuel properties and concentrations of ash-forming elements in fuels are in Appendix I & II. In addition, Figures 1-2 and **Figure 5** in **Paper VI** show molar ratios of some major ash-forming elements in the used fuels. For all fuels information on wood species is not available.

3.1.1 District heating boilers

The measurements were carried out in three boilers based on rotating grate technology (A,B,C) and in a gasification combustion boiler (D) (**Paper I**). The plants produced heat for district heating net and were fired with moist forest residues and saw mill residues (Appendix I). All plants were equipped with cyclones for separation of large particles from the flue gas. In addition, plants B and C were equipped with single field electrostatic precipitators (ESP) and plant A with a condensing flue gas scrubber. The test runs were carried out at constant load which were from 60 to 100 % of the nominal output.

The sampling locations were at the stack downstream of the cyclones. The temperatures in the sampling locations varied between 110 and 150 °C. In addition, at plants A, B and C, measurements were also carried out after secondary particle filters.

The aerosol measurements included determinations of fine particle mass concentrations (PM₁) total suspended particle concentrations (TSP), particle number concentrations and particle size distributions. Particle number concentrations and number size distributions were measured using electrical low pressure impactor (ELPI) (Keskinen et al., 1992). Particle mass size distributions were determined using Berner low pressure impactors (BLPI) (Hillamo and

Kauppinen, 1991). Particle samples were analysed for chemical composition. In addition, samples were collected for scanning electron microscopy (SEM). Gaseous compounds were measured with single-component analyzers, including O₂, CO₂, NO, NO₂, CO and SO₂.

The sample flow for fine particle sampling and analysis was diluted with dried, filtered and pre-heated air. The sample flow was first drawn through a pre-cyclone, to remove coarse particles from the sample, and then diluted in a porous tube diluter (Lyyräinen et al., 2004). The sample flows were divided between different analyzers and sample collectors as described in **Paper I**. CO₂ concentrations were measured from the diluted flue gas for the determination of the dilution ratio. The dilution ratios were 2.4-8.5 in the particle mass size distribution measurements (BLPI) and 10-26 in other particle measurements.

Table 1. Combustion appliances and fuels

Appliance	Reported in paper	Combustion technology	Nominal output	Operated output	Fuel
A	I, II, VI	Rotating grate boiler	5 MW	3.7-4.1 MW	Sawdust + bark
B	I, II, VI	Rotating grate boiler	15 MW	12.4-16.4 MW	Forest residue
C	I, II, VI	Rotating grate boiler	10 MW	6.9-8.2 MW	Sawdust + bark
D	I, II, VI	Crossdraft gasification boiler	7 MW	4.3-4.7 MW	Forest residue
E	VI	Moving step-grate boiler	500 kW	300-400 kW	Pellets (stem, bark, peat)
F	III	Top-feed pellet stove	8 kW	≈ 8 kW	Pellets (stem, bark)
G	V	Pellet/Cereal burner, updraught boiler	20 kW	9.3-16.4 kW	Cereals, Pellets (wood, peat), Pressed rape seed residue
H	IV	Laminar flow reactor, pulverized fuel combustion	-	0.57 KW	Wood powder

3.1.2 Pellet appliances

Experiments with the pellet stove (F) were carried out at the facilities of the University of Eastern Finland. In the stove, the pellets are supplied on a perforated cup from the top by a screw, and air is supplied from below the cup. The stove was operated with a nominal load. The fuels included pellets made of separate stem and bark materials of five Finnish wood species and one commercial pellet quality (Appendix I). Particle samples were drawn from an insulated stack at

temperatures between 99 and 165 °C to a low-pressure dilution tunnel, constructed according to the ISO 8178-1 standard. The dilution air was filtered laboratory air. The air flow in the tunnel was adjusted with a constant volume pump to approximately 670 m³/h (NTP). The DR was adjusted by setting the tunnel pressure by a valve in the dilution air inlet, giving DRs between 73 and 86. Samples from the tunnel were drawn for particle number concentrations and size distribution measurements (ELPI) and for PM1 filter sample collectors. Gaseous emissions were measured with a combination of single component analysers (ABB Cemas Gas Analysing Rack), including O₂, CO and NO and NO₂.

Appliance E is a 500 kW moving step-grate boiler used for heating a school. The boiler grate moves with a desired sequence and thus the fuel travels across the boiler. The boiler was operated with a 60-80 % load. The tested fuels included commercial pellets with stem material, bark pellets, wood pellets including both stem and bark materials and peat pellets. In addition, the boiler was equipped with two fuel silos and feeding systems to supply fuels as different mixtures to the boiler. In Appendix I and II these fuel mixtures are marked “Pellet mix”. The grate moving frequency was optimized for each fuel. For bark-free wood pellets, the grate moves occurred less than once per hour, while for bark- and peat-containing fuels the grate was set to move several times per hour.

The measurement setup for appliance E is shown in Figure 3. The fine particle sample was first drawn through a cyclone and then diluted in two steps. The first dilution took place in a porous tube diluter with preheated dilution air (180 °C) and the second in an ejector diluter (Dekati Ltd.). The porous tube diluter construction is similar to the one described by Lyyränen et al. (2004). The dilution air was dried and filtered for particles and hydrocarbons. The dilution ratio was defined by the measured CO₂ concentrations in the diluted sample. Fine particle measurements included number size distribution measurements using ELPI and Fast mobility particle sizer (FMPS, TSI), mass size distribution measurements using a Dekati low pressure impactor (DLPI, Dekati Ltd.) and PM1 filter sample collections. The TSP emissions were measured by in-stack filter collections. Gas-phase composition in the stack was measured using a FTIR multi-component analyser (Gasmeter).

Appliance G is a tube burner suitable for burning both pellets and cereals. The burner was connected in a conventional up-draught boiler. The experiments were carried out in the facilities of the Finnish Work Efficiency Institute. The fuels included oat seeds, rape seeds, pressed rape seed residues and wood pellets. In addition, peat pellets and kaolin were mixed with some of the fuels (Appendix I). The setup for fine particle and flue gas composition measurements was the same as for appliance E.

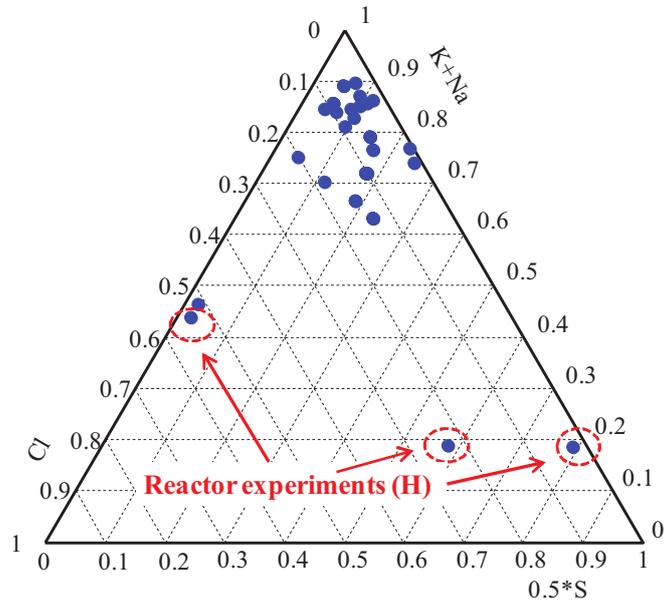


Figure 1. Molar ratios of K, Cl and S in the fuels.

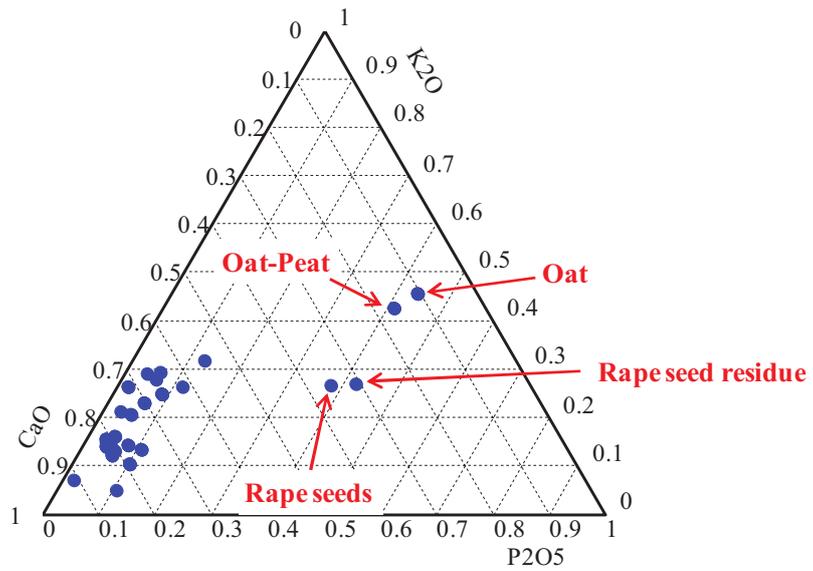


Figure 2. Molar ratios of P, K and Ca in the fuels given as oxides.

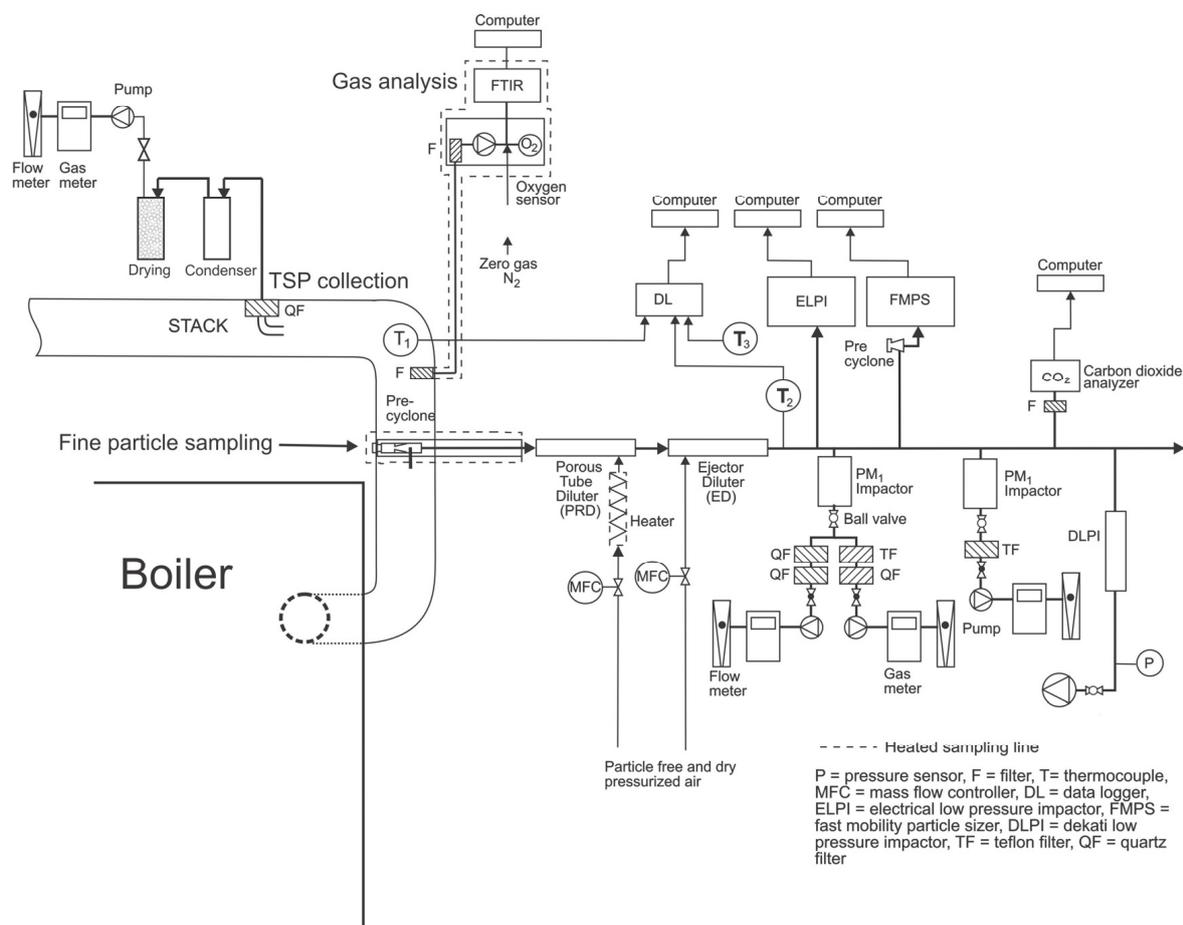


Figure 3. The measurement setup during experiments with appliance E.

3.1.3 Laminar flow reactor

Pulverized wood combustion experiments were carried out in a laminar flow reactor at the University of Eastern Finland to study the effects of fuel chlorine and sulphur on fine particle formation and ash release (**Paper IV**). The fuel was fine dried wood powder originating from the veneer grinding process of a plywood factory. The fuel was supplied into the reactor via a thin nozzle as preheated air suspension, giving a stable combustion process. Pre-heated secondary air was supplied around the nozzle. The reactor walls were heated to 1150 °C. The fuel supply was 30 mg/s, which corresponds to a power of approximately 570 W. Different amounts of chlorine were supplied as HCl gas into the secondary air and sulphur as SO₂ gas into the fuel suspension.

The fine particle samples were drawn from the reactor with a movable porous tube diluter specially designed for the reactor setup. The sampling system has been described and characterized by Sippula and Jokiniemi (2009). The sampling temperature was around 850 °C

during the experiments. An ejector diluter (Dekati DI-1000) was used for secondary dilution of the sample. The measurements included fine particle number size distribution measurements with two Scanning mobility particle sizer setups (SMPS, TSI) and with the ELPI. PM1-filter samples were collected for chemical analyses. In addition, particle samples were collected for SEM.

3.2 Particle characterization

3.2.1 Particle number and number size distribution measurements

Particle number concentrations and size distributions were measured using the Electrical low pressure impactor (Dekati Ltd.) (Keskinen et al., 1992), which measures particles with a fast response time in the size range of 30 nm - 10 μ m as aerodynamic diameter. Particles entering the ELPI are first charged and then collected in the low-pressure impactor according to their inertia. When particles hit the impactor stages, they become discharged. This current is measured by electrometers that are connected to the impactor stages. The measured current distribution is then converted to particle number size distributions. In this work, four different ELPI setups were used. First, in the experiments with appliance F, the ELPI included a 30 lpm impactor with aluminium substrates. Second, with appliances G and H, a 10 lpm impactor with sintered stainless steel impactor plates was used. Third, in appliances A to D the ELPI was equipped with a 10 lpm impactor with Al-substrates and additionally with a filter stage for measuring particles below the lowest impactor stage cut-off size. Finally, with appliance E, a 10 lpm impactor with sintered substrates and an additional filter stage were used.

Scanning mobility particle sizers (SMPS, TSI) were used in the measurements for **Paper IV**. In SMPS, the particles are first charged and then conducted in a differential mobility analyzer (DMA), which classifies the particles according to their electrical mobility, using a high-voltage electric field. The classified particles are counted using a condensation particle counter (CPC). As a result, good particle size resolution can be achieved. In this work two different SMPS configurations were used. The Long-SMPS configuration included TSI DMA 3071 and TSI CPC 3022, with a particle size detection range of 14-735 nm. The Nano-SMPS configuration included TSI DMA 3085 and TSI CPC 3025, with a particle size detection range of 3-79 nm.

A fast mobility particle sizer (FMPS, TSI) was used in the measurements with appliances E and G. Particles entering the FMPS are first charged and then conducted in a cylinder with a high-voltage electric field. The particles are displaced from the flow onto the cylinder walls according to their electrical mobility. The cylinder walls are connected to electrodes to measure the current given by the particles. The measured current distributions are further converted to particle number distributions. The FMPS measures particles in the size range 5.6 – 560 nm.

The selection of the measurement device for particle size and number analysis is important, since different analyzers have different benefits and disadvantages. The advantages of

ELPI are good time resolution, which allows the observation of relatively short temporary changes or fluctuation in the process, and a wide particle size range. For these reasons ELPI was used in all of the measurements. Since ELPI measures particles as aerodynamic size, knowledge of the particle effective density is needed if one wants to convert particle size to Stokes size. The advantage of SMPS and FMPS is the high size resolution of fine particles. In addition, the measured mobility size is practically equal to Stokes size, and not dependent on the particle effective density. The FMPS also has a very fast time response and it is therefore very well suited to measure fast changes in the process. In an ideal case both aerodynamic particle size and mobility or real particle size can be measured, which also gives information on the particle effective density (Kelly and McMurry, 1992, **Paper III & V**).

3.2.2 Particle mass and mass size distribution measurements

The fine particle mass (PM₁) concentrations were determined from either filters or impactor substrates. The filter samples were collected on Teflon (PTFE) filters. Pre-cut impactors (Dekati PM10) were used to remove particles larger than 1 µm in diameter from the sample flows. The filters were weighed with a microbalance (Mettler Toledo MT1). The weighing procedure is explained in detail in Tiitta et al. (2002).

Low-pressure cascade impactors were used for measurements of particle mass size distributions and particle mass concentrations. The impactors used were Berner-type low pressure impactors with 11 stages (BLPI) (Hillamo and Kauppinen, 1991) and a Dekati low pressure impactor (DLPI) with 13 stages (Dekati Ltd.). The impactors classify particles in different size fractions according to the particle inertia. The collection substrates were made of polycarbonate (Nuclepore) in the BLPI and of aluminum foil in the DLPI. The substrates were greased to avoid particle bounce from the collection stages. Substrates were weighed before and after sample collections, similarly to the PM₁ filters.

3.2.3 Chemical analyses

Analyses of inorganic species were made from the PM₁ Teflon filter samples and BLPI impactor substrates. Elemental analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) included analyses of Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, Tl, U, V and Zn. Water-soluble ions were analysed by ion chromatography (IC) that detected SO₄, NO₃, Cl, PO₄, Br and F.

Fine particle carbon fractions were analysed from PM₁ quartz filter samples using a thermal-optical carbon analyser (Sunset Instruments). The analyser measures the amounts of organic and elemental carbon in the sample (Turpin et al., 2000). The analyses were performed according to the NIOSH Method 5040 (NIOSH, 1999). The artefact caused by adsorption of

gaseous organic compounds into the filter material was corrected using a back-up filter. The issue has been described by McDow and Huntzicker (1990) and by Turpin et al. (2000). In addition, the amounts of carbonate carbon were estimated according to the NIOSH protocol as described in **Paper III**.

The fuels fired in the combustion tests were analysed for their ash content, moisture, heating values and ash-forming elements. In addition, bottom ash samples from some of the locations were analysed. The methods used in the ash analyses include ICP-MS, ICP-atomic emission spectrometry (ICP-AES), ICP-optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF). Different digestion methods were used in the fuel analyses. Some of the samples were prepared according to EPA-standard based digestion with HNO₃ and microwaves (EPA, 1994) (**Paper I**). Most of the fuel samples were ashed and dissolved with mixtures of HF and HNO₃ (**Paper IV, V**) or H₂O₂ and HNO₃ (**Paper III, V**). In addition, some of the samples were additionally dissolved directly with a mixture of HF, HNO₃ and H₂O₂ (**Paper VI**). Different sample digestion methods are discussed in detail in Baerenthaler et al. (2006).

3.2.4 Observation of particle morphology

Scanning electron microscopy was used for viewing particle shape and morphology. The instruments used were the SEM, Leo DSM 982 Gemini at the VTT Technical Research Centre of Finland, and XL30 ESEM TMP at the University of Eastern Finland. The SEM at VTT is capable of the high magnifications required for studies of fine particle morphology, while the SEM at the University of Eastern Finland was used to study coarse particle properties in pulverized fuel combustion (**Paper IV**). Both of the instruments were equipped with energy dispersive spectroscopy (EDS), which provides the possibility to analyze particle chemical compositions.

The samples were collected on holey carbon copper grids by thermophoretic sampling or by suction sampling, and on graphite substrates using an electrostatic collector. In thermophoretic sampling, a cool grid is exposed to hot flue gas. The temperature difference causes a thermophoretic drift, which is independent of the particle size for fine particles (Marple et al., 2001), and particles are transferred on to the cool surface. In suction sampling, a tiny sample flow is drawn through a grid. The electrostatic collector is described by Flagan (2001).

3.3 Thermodynamic equilibrium calculations

Calculations of global thermodynamic equilibria at high temperatures were carried out to help in the interpretation of the experimental findings on fine particle chemical composition. The method is based on the Gibbs free energy minimization in a multiphase system. The main goal in the calculations was to estimate the gas-to-particle conversion temperatures of fine fly ash-forming elements in the cooling flue gas, and to determine which chemical compounds are most likely

present in fine particles. The calculations were restricted to oxidizing conditions and to take into account only the species in the PM1 fraction. This procedure is based on earlier work which shows that fine ash particles are formed mainly of vaporized ash species released from the fuel, while larger particles are mechanically produced (Valmari et al., 1998, Lind et al., 2000), and that, based on mass transfer aspects, the interaction of ash-forming vapours with large fly ash particles is negligible in practical combustion systems (Jokiniemi et al., 2001). An exception to this is fluidized bed combustion (not studied in this work), where the bed sand affects the vaporized species (Lind, 1999, Lind et al., 2000).

The species given as input were the major fly ash elements in the fine particle samples and the major gas-phase compounds: H, C, N, O, S, Cl, K, Na and Zn. The calculations were carried out using the Equilib-module in the FactSage 5.3 and 5.5 softwares. Thermodynamic data were taken from the software databases (Bale et al., 2002). The equilibria were calculated at temperatures between 300 °C and 1600 °C. All appropriate gaseous and condensed compounds and solution phases SALTA, CSOB and KNSO were included in the calculations. The solution phases provide data on non-ideal alkali metal salt solutions.

In general, when interpreting results from the equilibrium calculations, it should be kept in mind that the calculations do not consider limitations by reaction kinetics and imperfect mixing. In addition, many species with low concentrations are not included in the calculations.

4 RESULTS & DISCUSSION

4.1 Concentrations of particles and gases

Conventional wood fuels. Table 2 summarizes the emissions and combustion conditions in the appliances studied when operated with the currently most typical Finnish wood fuels. These include forest residues, saw mill residues and pellets made of wood stem material. The flue gas CO concentrations varied between 7 and 241 mg/MJ, indicating a relatively efficient combustion process in all of the appliances. The NO_x emissions varied between 33 and 156 mg/MJ and in some cases correlated with the fuel nitrogen content. The SO₂ and HCl concentrations were negligible in the combustion of wood fuels. This is because in wood fuels the (K+Na)/(Cl+2S) ratios are typically high (> 1) Thus, chlorine and sulphur are likely to be bound to alkali metal salts.

The observed generation of fine particles varied between 13 and 92 mg/MJ, and as number concentration between 1.2×10^{13} and 76×10^{13} particles/MJ. The largest PM1 values were measured in the grate firing of moist wood residues (55-92 mg/MJ, **Paper I**), in pulverized wood combustion (64 mg/MJ, **Paper IV**) and in a pellet stove with a cup burner (≈ 58 mg/MJ, **Paper III**). The PM1 in other pellet-fired appliances and in the gasification combustion boiler were clearly lower (13-17 mg/MJ).

The highest number concentration (7.6×10^{14}) and smallest mean particle diameter (GMD = 23 nm) were measured from the laminar flow reactor. This is due to the quenching of the sample at high temperatures (850 °C), which freezes chemical reactions, reduces particle coagulation and agglomeration and affects the nucleation/condensation dynamics of the condensable species (**Paper IV**).

Most of the boilers were equipped with particle filtration systems, including cyclones, electrostatic precipitators and a flue gas scrubber. The cyclones generally do not filter out fine particles, so they do not influence the PM1 results shown. The single field ESPs were found to remove around 95 % of PM1 in boilers B and C (**Paper I**) The spray-tower type flue gas scrubber removed on average 44 % of PM1 (**Paper I**).

Figure 4 shows a comparison of PM1 emissions in this study with the most comparable data available in the literature. The obtained PM1 values are on a similar level with those in the literature, except those from rotating grate-fired district heating boilers, which were higher than the literature values representing moving step grate technology. Differences in the results are expected since the boiler technologies and fuels are not identical. In addition, the sampling systems vary considerably, which can account for some of the differences.

Table 2. Emissions and combustion conditions, when operated with conventional wood fuels^a

Appliance	Combustion technology	Fuel	Sampling location	H ₂ O	O ₂	CO	NO _x (as NO ₂)	N ^b	GMD ^b	TSP ^c	PM1
				%	%	mg/MJ	mg/MJ	(1/MJ)	(nm)	mg/MJ	mg/MJ
A	Rotating Grate	Sawdust + bark	after cyclone, before scrubber	22	5.2	79 (± 77)	135 (± 9)	n.m.	n.m.	183	55
A	Rotating Grate	Sawdust + bark	after scrubber	17	5.1	68 (± 65)	132 (± 9)	1.7E+13 (± 2.1E+12)	132 (± 4)	54	31
B	Rotating Grate	Forest residue	after cyclone, before ESP	≈ 24	5	6.6 (± 0.6)	156 (± 4)	2.7E+13 (± 1.2E+13)	100 (± 9)	211	92
B	Rotating Grate	Forest residue	After ESP	≈ 24	5	n.m.	n.m.	6.1E+11 (± 3.4E+11)	147 (± 7)	16	6.0
C	Rotating Grate	Sawdust + bark	after cyclone, before ESP	≈ 24	4.6	≈ 12	≈ 33	n.m.	n.m.	483	77
C	Rotating Grate	Sawdust + bark	After ESP	≈ 24	4.6	n.m.	n.m.	6.5E+12 (± 1.4E+12)	216 (± 7)	35	3.9
D	Gasification combustion	Forest residue	after cyclone	24	4	117 (± 304)	91 (± 8)	1.2E+13 (± 3.2E+12)	96 (± 15)	52	13
E	Moving step-grate	Stem wood pellets	after cyclone	9.9	7.5	37 (± 64)	52 (± 9)	2.0E+13 (± 2.4E+12)	64 (± 7)	22	17 (± 2)
F	Pellet stove	Stem wood pellets	Stack	≈ 9	16.3	142 (± 42)	85 (± 24)	5.1E+13 (± 1.8E+13)	141 (± 9)	-	58 (± 20)
G	Pellet/Cereal burner	Stem wood pellets	Stack	9.1	9	21 (± 16)	90 (± 9)	4.3E+13 (± 0.3E+13)	62 (± 3)	-	15 (± 2)
H	Laminar flow reactor	Wood powder	after flame (at 850 °C)	10.5*	3.8*	241 (± 200)*	134 (± 12)*	7.6E+14*	23*	-	64

^aStandard deviations of the results are shown in brackets when available

N = Particle number emission

^bMeasured with ELPI except Appliance H, which was measured with SMPS

^cMeasured with in-stack filter collection except appliance C, which was measured with a cyclone-BLPI combination

*Selected typical results from the reactor experiments

n.m. = not measured

Bark fuels. The effects of bark fuel materials on emissions were tested with pellets containing 20 to 100 % bark. The use of bark was found to increase the fine particle emissions in all cases. In the experiments with different bark materials in the pellet stove, the PM1 increased 3–10-fold and the particle number emission 1.4–2.7-fold, when compared with commercial wood pellets. The pine bark material produced the lowest PM1 among the bark fuels (**Paper III**). Similarly, in the step-grate boiler (E), the pine bark pellets generated a 1.6-fold PM1 when compared with pellets made of stem material (**Paper VI**). In addition, bark fuels emitted higher NO_x emissions due to their higher nitrogen contents. In the pellet stove, the PM1 emissions from different bark and stem fuels were found to correlate linearly with the fuel ash content, as also found by Wiinikka et al. (2005) in a laboratory reactor.

Peat and cereal fuels. Cereal fuels were studied with appliance G, including oat, rape seeds and pressed rape seed residue. Peat fuels were studied as pellets and mixed with oat

(appliance G) and with stem and bark wood pellets (appliance E). During the experiments with cereal fuels, optimal combustion settings were looked for. This resulted in relatively low emissions of incomplete combustion. The PM₁ of rape seeds was slightly lower than that of wood pellets, while rape seed residue and oat had 1.4- and 1.8-fold emissions, respectively. The mixing of peat with oat clearly increased PM₁ (**Paper V**). In contrast, in the pellet boiler experiments, adding peat to wood fuels was found to decrease PM₁ (**Paper VI**). The suggested reasons for these observations are discussed in section 4.4.

Burner settings. In the interpretation of the results, it should be considered that the settings of the appliance significantly affect the emissions. In the pellet stove, the combustion test were run with factory settings. Since the stove is designed for low ash content (≤ 0.5 % ash) pellets, the use of bark pellets with higher ash content in some cases considerably increased the products of incomplete combustion (CO, OC, EC). However, the extensive chemical analysis of PM₁ makes it possible to distinguish between the products of incomplete combustion and ash material released from the fuel, which helps in the interpretation of the results (Figure 6). In appliances E and G, the combustion settings were adjusted for each specific fuel to obtain as good combustion efficiency as possible. In these appliances, the products of incomplete combustion remained relatively low with all fuels (Figure 7).

4.2 Particle size and structure

Figure 5 shows a comparison of particle mass size distributions measured with different appliances and fuels. The distributions, measured at district heating plants, contained fine particle modes of 0.1–0.2 μm as aerodynamic diameter and a significant fraction of coarse particles ($d_p > 1 \mu\text{m}$). With smaller combustion appliances, most of the fine particles were slightly smaller in size and the fractions of coarse particles were typically small (**Paper V, VI**). However, an exceptional case is the laboratory pulverized wood combustion system, which generates high concentrations of coarse particles (**Paper IV**).

When comparing the mass size distribution results between different boilers, the effects of different sampling systems must be considered. While the sampling setup in the district heating boiler contained only one-step dilution in a porous tube diluter, the measurements in boilers E and G were equipped with two-stage dilution, with porous tube dilution as the first stage and an ejector diluter as the second stage. The porous tube diluter is likely to have low particle losses due to its construction, and sheath air preventing deposition and thermophoresis (Auvinen et al., 2000). The ejector diluter is known to have high losses for coarse particles but relatively good transport efficiency at least for particles below 2 μm in aerodynamic diameter (Wierzbicka et al., 2005). Thus, the coarse particle fractions in the particle mass size distributions measured from appliances E and G could be biased by the sampling system. Nevertheless, the comparison of in-

stack TSP and PM1 measurement data from appliance E shows that there were not significant amounts of coarse particles in the flue gas.

The particle number size distributions were mainly unimodal. The geometric mean particle diameters (GMD) downstream of heat exchangers, based on number size distributions, varied from 58 to 188 nm. Uncertainty in the size analysis is caused by different measurement setups of ELPI. The use of sintered plates as impactor substrates has been observed to result in smaller particle size than aluminium plates (Tissari et al., 2005), which may explain some of the observed differences.

Samples for scanning electron microscopy were collected from Appliances A, C, F and H. The fine particles were either single primary particles or agglomerates of a few primary particles with relatively compact structure (**Paper I & III**). The pulverized wood combustion produced coarse particles with varying shapes, which were probably ash residues of the fuel particles.

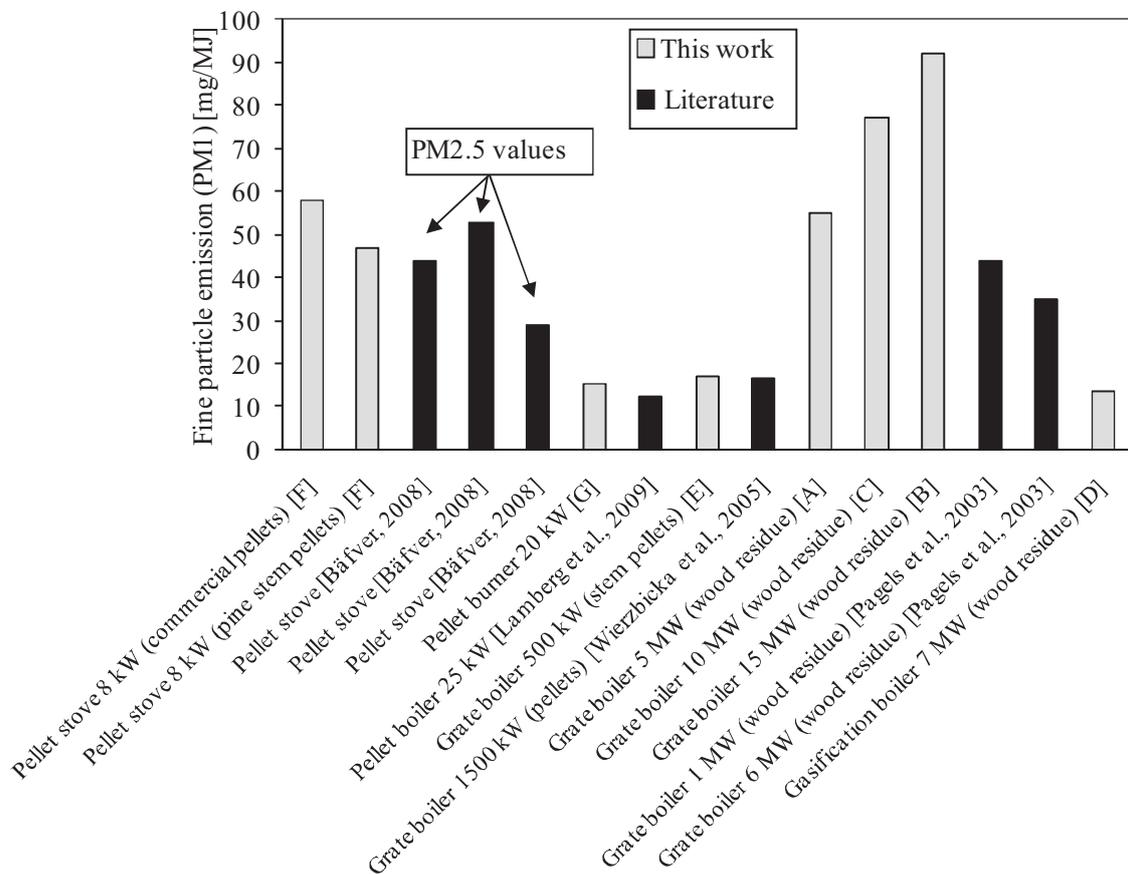


Figure 4. Comparison of fine particle emission results with those in the literature. The results are measured upstream of possible fine-particle removal devices, but downstream of cyclones (if existing).

4.3 Fine particle chemical composition

The PM1 chemical compositions were dominated mainly by potassium, sulphate and chloride (Figure 6). In addition, in most of the samples, considerable fractions of zinc, sodium and carbonate could be identified. The observed PM1 inorganic material compositions agree well with those in the other studies on fine particles formed in wood combustion (Brunner, 2006, Valmari et al., 1998, Pagels et al., 2003). The cereal fuels differed from wood fuels by generating large fractions of PO₄ in the PM1 (**Paper V**), which was also found by Bävfer et al. (2009). Furthermore, the laboratory pulverized wood combustion setup produced large amounts of Ca and Mg in the PM1 (**Paper IV**), which is not observed in grate combustion units. The fractions of chloride and sulphate varied largely. The use of sulphur-rich fuels increased the amount of sulphate and decreased chloride in PM samples (discussed more in section 4.5). The amounts of PM1 carbon, originated from incomplete combustion (EC and OC), varied between different appliances and fuels. Their concentrations indicate the efficiency of the combustion process. Considerable fractions of EC and OC were formed in appliance F (pellet stove) with some of the high ash content fuels (Figure 7 and **Paper III, Table 3**). With other fuels and appliances, the OC+EC fractions were below 6 mg/MJ, and constituted 0.8–22 % of the fine particles. These values are on a similar level with the carbon emissions from small wood-fired district heating boilers reported by Wierzbicka et al. (2005). The OC/EC ratios varied largely. In grate boiler E, the carbon emission was mainly as EC, while for other appliances the OC/EC ratios were close to unity or the OC fraction dominated the carbon emission.

Trace metals. The measured PM1 trace metal concentrations are shown in Appendix III. The elements other than Zn belong to the so-called “dirty dozen” and the air emissions of these elements are limited for waste combustion according to the European Waste Incineration Directive (Directive 2000/76/EC, 2000). The fuels contained considerable concentrations of Zn and Mn while other elements were present only in relatively low concentrations. Zn, Pb, Cd, Cu, As and Tl were found to enrich in the fine particle fraction. In contrast, Mn was found clearly to remain in the coarse ashes, except in the laboratory flow reactor with pulverized wood combustion. In addition, considerable release fractions of Ni and Cr were found in the PM1, as was also reported by Jimenez et al. (2008). However, contamination of these elements from the metal surfaces in the sampling system cannot be excluded. The results agree qualitatively with those of other studies on fixed bed combustion (Oberberger et al., 2001, Brunner, 2006, Lundholm et al., 2007) but differ from those of studies on fluidized bed combustion, where the high amounts of coarse ashes effectively capture volatilized metals (Lind et al., 2000).

In general, the results show that alkali metal compounds dominate the formation of fine particles in continuously fired appliances. However, the EC, OC and metal fractions may significantly influence the health effects of the particles. Furthermore, the fine particle optical properties are considerably affected by carbon fractions.

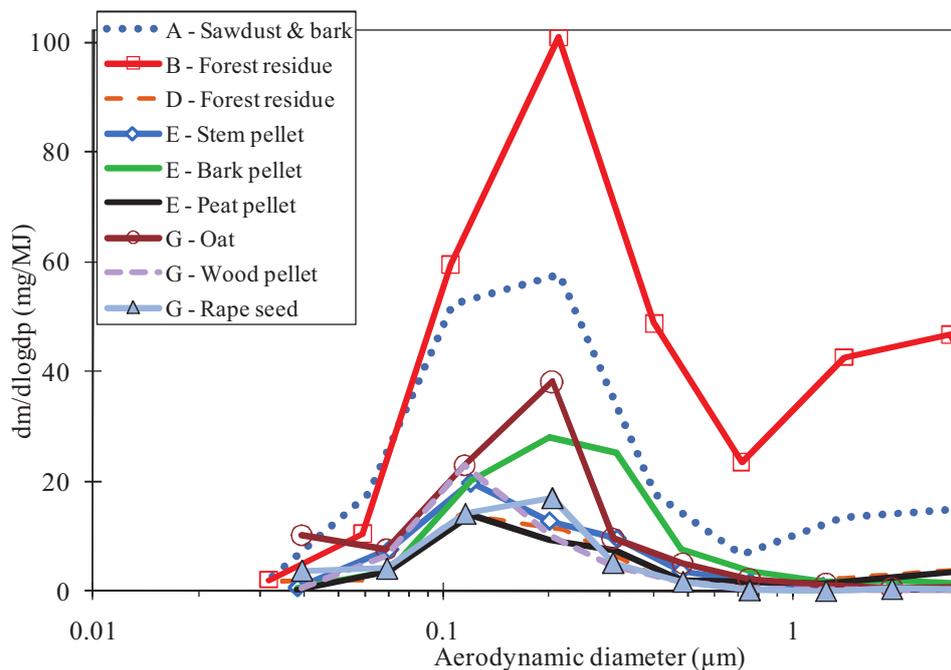


Figure 5. Particle mass size distributions from various appliances and fuels. Results from appliances A and B are upstream of secondary particle filters.

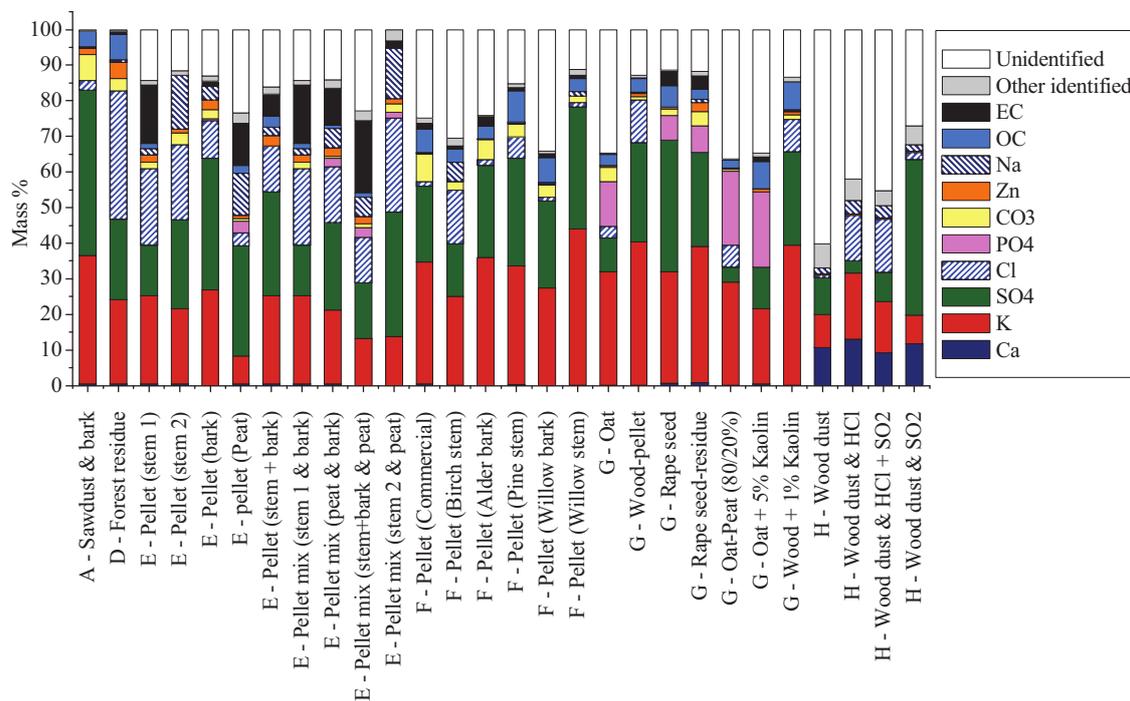


Figure 6. PM1 chemical compositions. Results from appliance H contain no data from carbon analyses, and those from appliance F no cations other than K, Na, Ca and Mg.

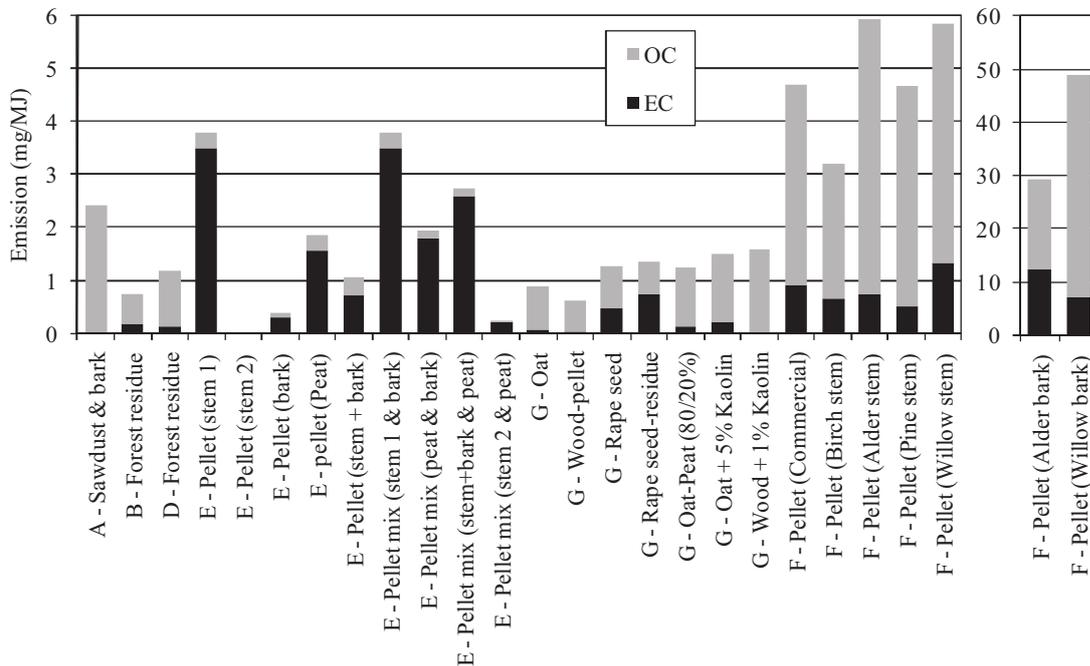


Figure 7. Elemental carbon (EC) and organic carbon (OC) in PM1 emissions.

4.4 Release of ash-forming elements

The applied method. Fractions of ash-forming elements in fine particles and gas-phase, as a percentage of the total amount supplied with the fuel into the process, were calculated based on chemical analyses made from fuel and fine particle samples. It should be noted that the results only give an indication of the release behavior of ash-forming species and contain some uncertainties. First, the method applied in this work is rather sensitive to uncertainties in the chemical analysis and in the sampling system. In most cases uncertainty is caused by varying fuel properties especially in the largest appliances of the study. Second, the released fractions are measured from cooled flue gas, except in **paper IV**, and are therefore affected by losses in the flue gas passage. However, the method gives an indication of the release behavior of elements and makes it possible to compare ash behavior between different fuels.

Alkali metals. The release of alkali metals showed both fuel- and appliance-specific release behavior (Figure 8). For the combustion of wood pellets made primarily of stem material, the release fractions of PM1 potassium in the flue gas were between 15 and 20 %. With pellets containing bark and peat materials, the fractions were clearly lower, ranging from 2 to 11 %. The K-release was found to be in correlation with the fuel Si-content (Step-grate boiler, **Paper VI**, **Figures 6 & 7**). In addition, the K-release was found to have a trend with fuel sulphur and chlorine concentrations (Step-grate boiler, **Paper VI**, **Figure 8**). Wiinikka et al. (2007) found

similar differences between the potassium release of wood pellets with low Si-content (12 % K released) and bark pellets (5 % K released). The observed release fractions were, however, lower than found in this work.

The K-release measured in pulverized fuel combustion, with fuel composition comparable to stem-pellets, was around 25 %. For district heating boilers firing moist forest residue, a clear difference was found between grate firing and gasification combustion. The K-release fraction calculated from the grate firing was around 8-fold that of gasification combustion (**Paper I**). This is probably due to the highly staged combustion in the gasification boiler, leading to lower temperatures in the fuel bed. However, the fuels were not identical and therefore this observation should be confirmed in a more controlled environment. A similar effect of air-staging on ash release was found by Lamberg et al. (2009) in a laboratory pellet boiler.

For oat- and rape-containing fuels, very low release fractions (1.3–3 %) of alkali metals were found in the PM1. The release was found to be associated with the release of chlorine in PM1 (**Paper V**). Probable reasons for the low alkali release with cereal fuels may be the high silicate content in the fuel, relatively high sulphur/chlorine ratios and high phosphorus contents, which may decrease alkali release by forming mixed phosphates in the bottom ash (Sandström, 2006). The release behavior of Na was similar to that of K, with only some exceptions.

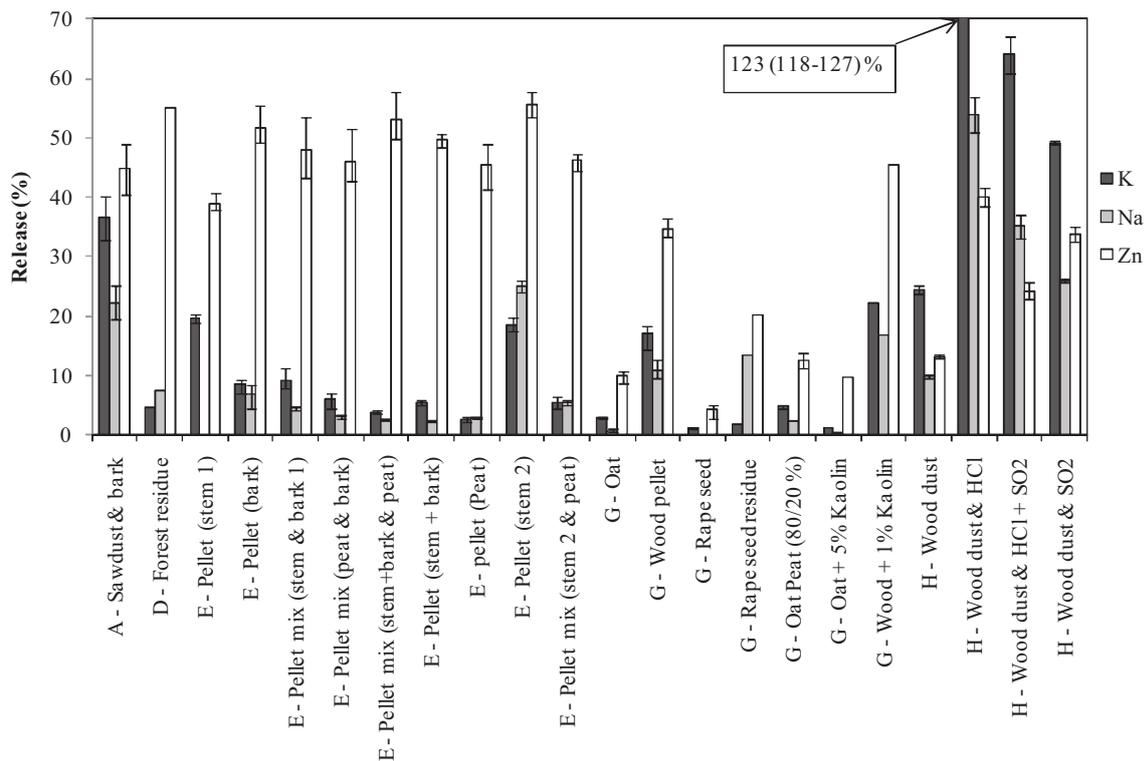


Figure 8. Release of K, Na and Zn in fine particles. The minimum and maximum values are shown with error bars.

Chlorine and sulphur. Chlorine and sulphur were generally released in high fractions into PM1 and gas-phase (Figures 9 and 10). With fuels containing only wood materials, large fractions of chlorine and sulphur in relation to the total amount were found in the PM1. In contrast, for cereal fuels and peat-containing fuels most of the fuel S and Cl were found as HCl and SO₂ in the flue gas. This was due to the excess of chlorine and sulphur in relation to alkali metals in the fuel (see (K+Na)/(Cl+2S) ratios in Appendix II). In some of the experiments considerably lower than 100 % release fractions were observed for S and Cl. In the case of S, calcium affects sulphur release by forming CaSO₄ which does not vaporize (Knudsen et al., 2004b). In addition, alkali sulphates have been identified from the bottom ash samples (Gilbe et al., 2008). Chlorine is generally believed to be released almost entirely into the flue gas in biomass combustion (Knudsen et al., 2004a). Since HCl is a very reactive gas, its sampling may include significant losses. In addition, some chlorine is often found in bottom ash and in coarse fly ash particles. The compounds may be calcium chloride (Coda et al., 2001) and in some cases alkali chlorides (Gilbe et al., 2008).

Zinc. Zinc was found to be released in PM1 in relatively high fractions (Figure 8). The Zn-fractions observed in the PM1 of wood-fired boilers varied between 35 and 55 % and were on a similar level with those observed by Wiinikka et al. (2007). The release seemed to be independent of the fuel ash composition in the tests with the moving step grate pellet boiler (**Paper VI**). In addition, no significant difference was found between grate firing and gasification combustion (**Paper I**). However, in the tests with cereal fuels and pulverized wood combustion, the zinc release was found to be associated with chlorine release in PM1 fraction, which may be related to the formation of ZnCl₂. The cereal fuels were found to release lower amounts of Zn than wood fuels (**Paper V**). The mechanism for the retention of zinc may be the formation of zinc silicates and zinc aluminium oxides (Struis et al., 2004). In this work, no correlations between zinc release and fuel silicates or fuel aluminium were observed.

Effects of added Cl and S. The effects of added HCl and SO₂ on ash release were tested in the experiments with pulverized wood combustion in a laminar flow reactor (**Paper IV**). The addition of Cl was found to clearly increase the release of alkali metals and many other metals. Moreover, the increase of sulphur was found to decrease the effect of chlorine. The addition of only sulphur was observed as higher concentration of ash-forming elements in PM1 but with only very small effects on fine particle number size distributions when compared with wood combustion without additives. The results indicate that an addition of chlorine converts alkali species into chlorides, which increases their volatilisation. The addition of sulphur in chlorine-rich combustion indicated an increase in the alkali sulphates in fuel particles and remaining coarse ash residues, which decreased alkali release into the fine particle fraction. The sulphation may occur on the surface, or in the boundary layer of the fuel particle (**Paper IV**). These findings are qualitatively in agreement with those in the experiments in real combustion appliances with

fuels of varying S/Cl ratios (**Paper VI**) as well as with those of other similar combustion reactor experiments (Lind et al., 2006, Miller et al., 2003).

Effects of silicates. The silicate-rich fuels (peat, cereal fuels) were found to release low fractions of alkali metals. In addition, in the experiments with various stem, bark and peat materials, the silicate content in the fuel was found to have a clear trend with the alkali metals released in the PM1 fraction, and the fraction remained in the bottom ash (**Paper VI**). One probable explanation for this is the formation of alkali silicate compounds (Lindström et al., 2008) that remained in the bottom ash. However, the fuel chlorine/sulphur ratio was also found to correlate with the amount of released alkali metals. Since peat especially is rich in both sulphur and silicates, the observed decrease in the release may be a combination of both of these effects. Thus, the addition of peat to wood fuel was found to decrease PM1 emissions due to a lower alkali metal release. On the other hand, it may increase problems with slagging, due to the lower melting point of ash (**Paper VI**). Further, the potential effect of silicates was studied with an aluminium silicate additive (Kaolin). The addition of 5 % kaolin to oat clearly decreased the release of potassium and increased the fractions of S and Cl in the gas phase (**Paper V**), probably due to chemisorption of potassium into aluminium silicate (Eq. 1 & 2, page 15). The potassium emission decreased by 59 % and PM1 emission by 38 %. The results agree very well with those of recently published experiments by Bävfer et al. (2009), which also included kaolin addition to oat combustion. In contrast, the addition of 1 % kaolin in wood pellets slightly increased the release of potassium and clearly increased the PM1 emission. The observed increase may be because of changes in the combustion conditions due to the increased ash content of the fuel. These findings can be compared with those of Tran et al. (2004), who carried out wood combustion experiments with very high kaolin additions (20 % and 40 %) The additions increased alkali release during the devolatilisation stage but decreased it during the char combustion stage, leading to an overall decrease in potassium release. The addition of peat to oat increased the release of K, Cl, S and also P. This was suggested to be due to the increased combustion temperature (**Paper V**).

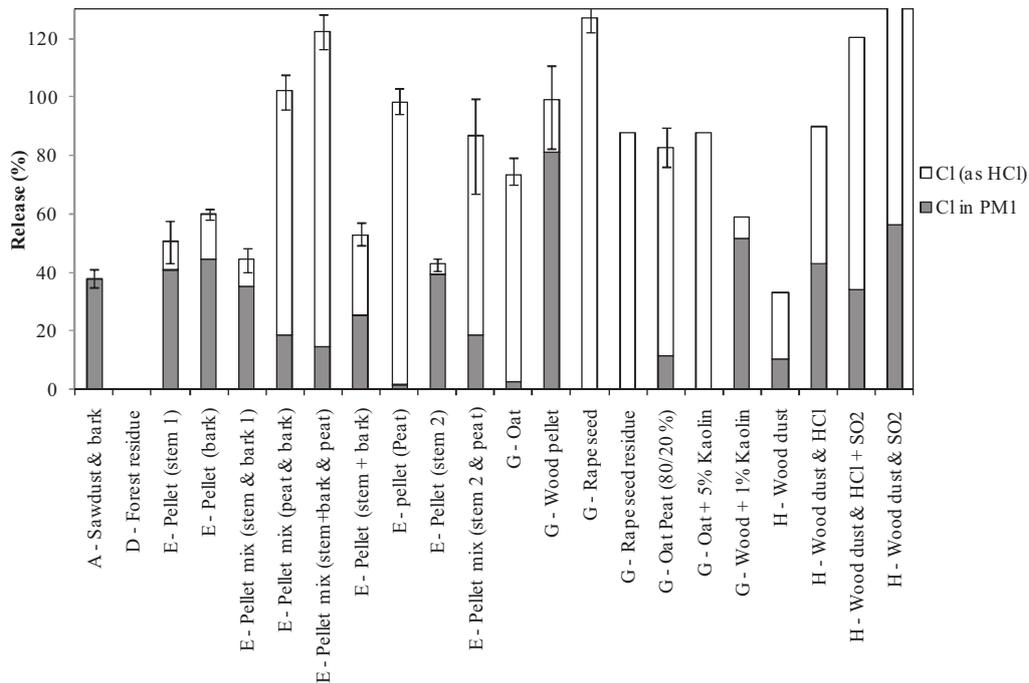


Figure 9. Release of chlorine in fine particles and gas-phase. The minimum and maximum values are shown with error bars.

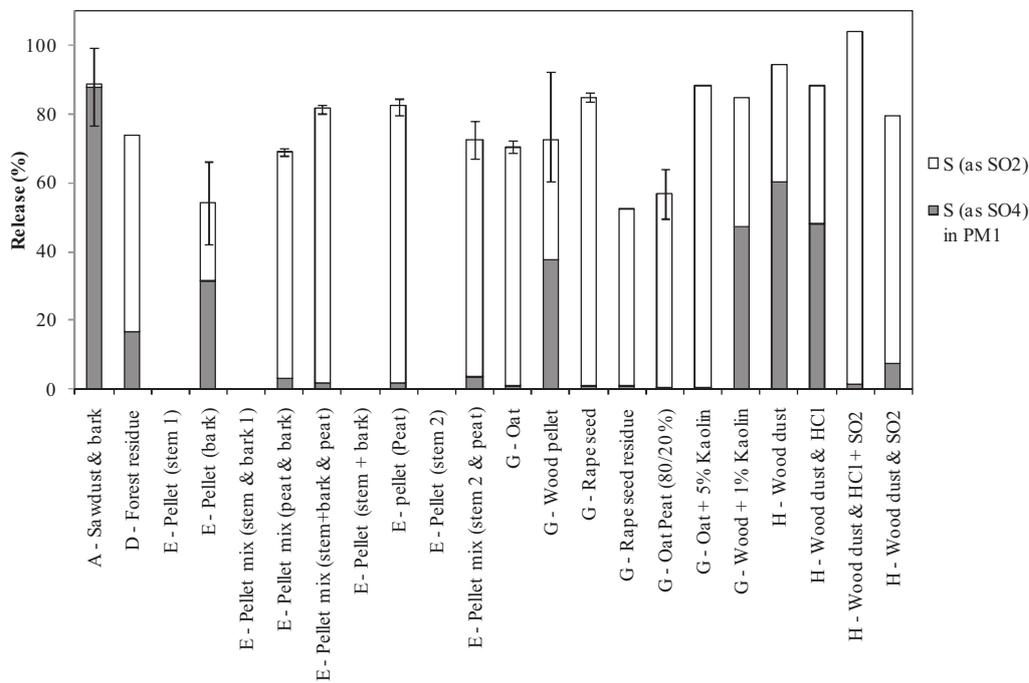


Figure 10. Release of sulphur in fine particles and gas-phase. The minimum and maximum values are shown with error bars.

4.5 Formation of fine ash particles

Thermodynamic equilibrium calculations were used to help in the interpretation of the experimental data on PM1 chemical compositions. The results of all calculated cases are summarized in the following paragraphs. Figures 11–13 show the calculated vapours phase concentrations of K, Na and Zn and Figure 14 shows an example of a typical calculation result with wood fuel.

At temperatures above 1100 °C, alkali metals are likely to occur as chloride vapours (KCl, NaCl, (KCl)₂, (NaCl)₂) and hydroxide vapours (KOH, (KOH)₂, NaOH, (NaOH)₂) in most of cases. This is in agreement with alkali release measurements made by Baxter et al. (1998). An increase of chlorine into the system increases the amount of alkali chloride vapours at the cost of alkali hydroxides. Likewise an increase in H₂O increases the amount of alkali hydroxides at the cost of chlorides. In addition, very small fractions of K and Na as elemental vapours are stable. At low oxygen concentrations this fraction increases and thus, based on equilibrium, some of the alkali metals may be released also as elemental vapours.

Below temperatures of around 1100 °C the formation of alkali sulphates is favoured if sulphur is present in the system. In a sulphur-rich system with low amounts of chlorine, alkali sulphate vapours may already be formed at higher temperatures (**Paper IV**, case D).

After sulphate formation, the alkali metals are likely to occur as chlorides. If the (K+Na)/(2SO₄+Cl) molar ratio is larger than one, the excess alkali metals, not bound to sulphates and chlorides, are likely to form carbonates. A limitation in the carbonate formation may lead to the formation of nitrates (**Paper III**), or condensed hydroxides may be left.

With phosphorus-rich fuels, alkali phosphates are likely to be formed (Wiinikka et al., 2007). Theoretically, these alkali metal compounds may further convert to sulphates, leaving phosphoric acid in the flue gas. As an indication of this, large amounts of phosphate in excess of cations was found in some of the cereal combustion experiments (**Paper V**). Since the thermodynamic data regarding high temperature phosphate chemistry is known to be inadequate, this result should be treated with caution.

Zinc is likely to occur as Zn vapour above temperatures of 1100 °C. With the fine fly ash compositions of this study it forms ZnO below this temperature, which leads to gas-to-particle conversion. This can be the first fine fly ash particle formation step with woody biomasses. In addition, in chlorine-rich systems, significant fractions of ZnCl₂ may be formed (**Paper IV**). ZnCl₂ condenses at significantly lower temperatures than ZnO. In addition, condensed phase Zn-sulphates can be formed.

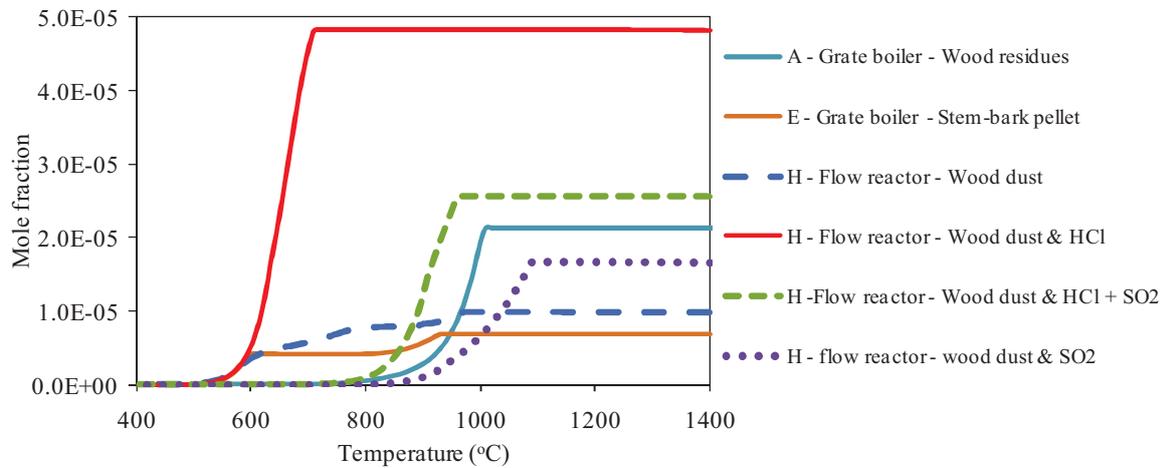


Figure 11. Calculated potassium mole fraction in the gas-phase.

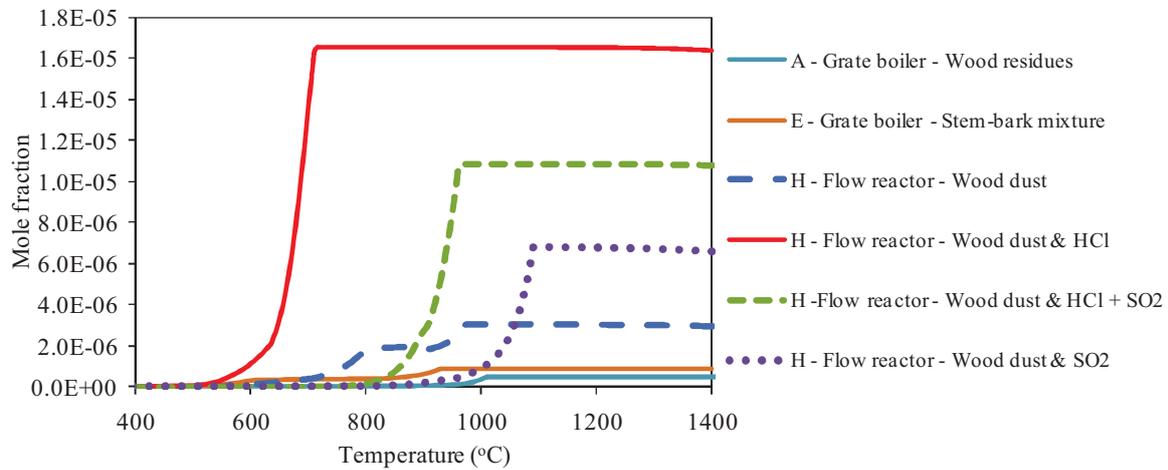


Figure 12. Calculated sodium mole fraction in the gas-phase.

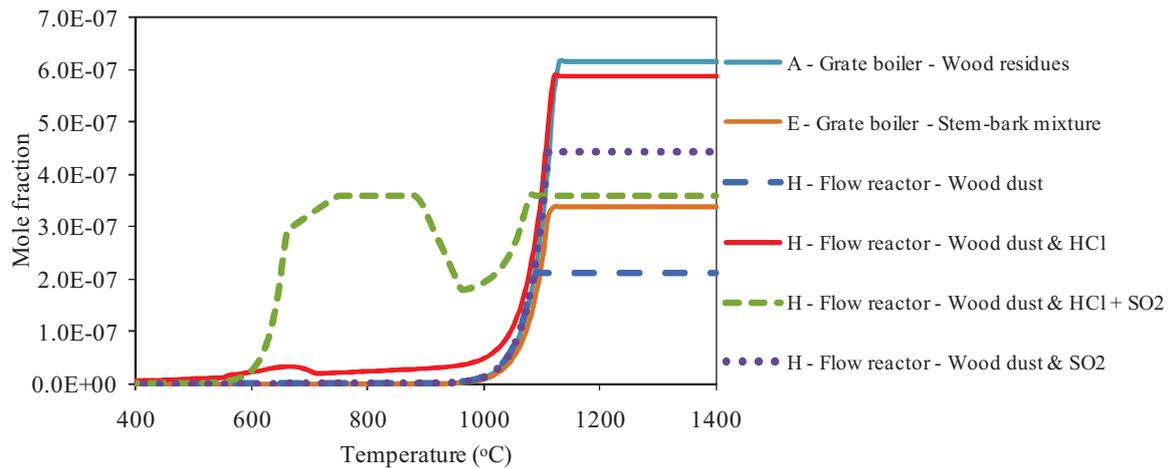


Figure 13. Calculated zinc mole fraction in the gas-phase.

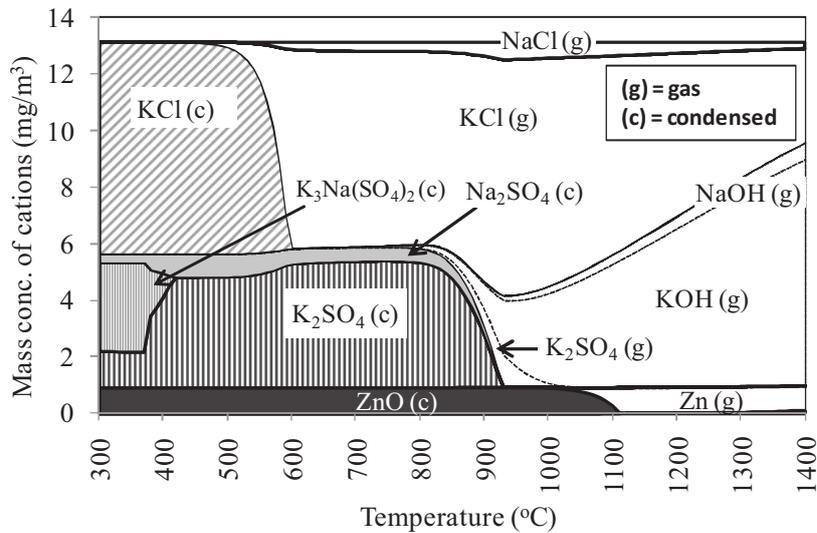


Figure 14. Calculated composition of fine fly ash according to equilibrium calculations (Appliance E, stem-bark mixture).

In the combustion of wood- and peat-containing fuels, the fine particles were composed mainly of K, SO₄, Cl, Na, Zn, CO₃, organic material and elemental carbon (EC). Smaller amounts of NO₃, PO₄ and a variety of different metals were identified in the samples. According to the equilibrium calculations, the alkali metals are likely to occur as sulphates, chlorides and carbonates. The zinc forms mainly ZnO except with fuels with high chlorine and sulphur contents. With these fuels, Zn may form large fractions of ZnCl₂ or Zn-sulphates.

Soot particles are formed already in the flame. This is followed by gas-to-particle conversion of the volatilized ash species which, according to the equilibrium, occurs in the temperature range of 500–1100 °C. With temperatures relevant to biomass combustion, ZnO can be the first significant vapour-phase compound forming condensed species in the flue gas. Nucleation of Zn has been suggested to form the first fine fly ash particles in the flue gas (Oberberger et al., 2001, Jöller, 2007). At a temperature range of 800–1100 °C, the formation of alkali sulphates occurs presumably throughout gas-phase sulphation reactions (Eq. 4 & 5, page 20). Alkali sulphates are estimated to nucleate or condense on existing seed particles soon after their formation. The remaining alkali chloride vapours condense at significantly lower temperatures. Furthermore, any remaining alkali hydroxide vapours are likely to form alkali carbonates. Finally, the gas-to-particle conversion of organic vapours occurs at varying temperatures. According to thermal optical analyses and the literature, the organics condense mainly below the temperature of 600 °C (Lipsky and Robinson, 2006). Figure 15 illustrates the formation pathway of particle emission in wood combustion. With annual plant biomasses and other phosphorus-rich fuels, the effects of phosphate may considerably affect the ash chemistry and also the fine fly ash particle formation. However, the role of phosphorus is still poorly

understood. The possible pathways of potassium are outlined in Figure 16. The figure offers a viewpoint on the possible reactions of phosphorus with alkali metals.

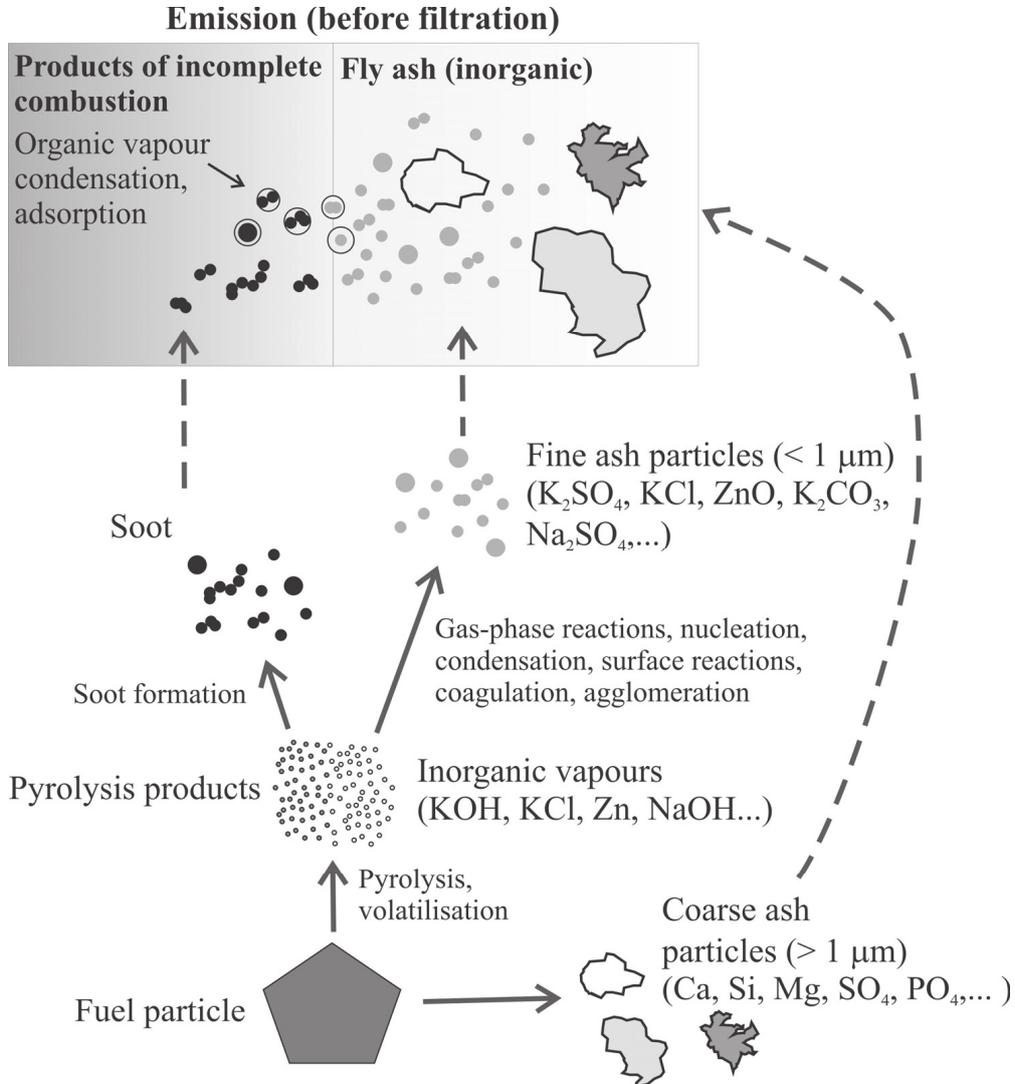


Figure 15. Particle formation in wood biomass combustion.

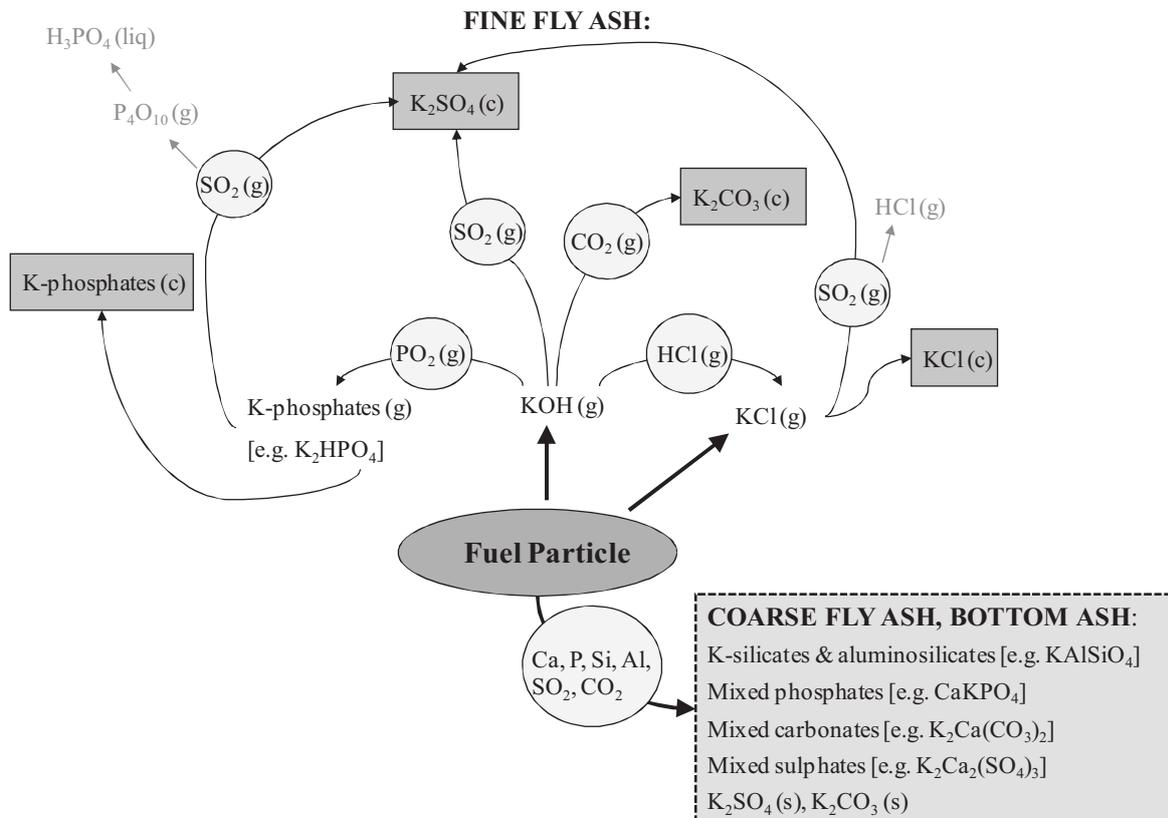


Figure 16. Simplified scheme of the possible pathways of potassium in biomass combustion. Intermediate reactive compounds are shown as “○” and fine fly ash compounds as “□”.

4.6 Comparison of emissions from biomass and heavy fuel oil combustion

Many fossil-fuel fired heating units are being replaced with biomass-fired plants in Finland and in other parts of the world. The flue gas emissions of district heating units operating with heavy fuel oil, wood residues and pellets were compared (**Paper II, Paper VI**). The PM1 emissions from HFO combustion varied between 4 and 8 mg/MJ and were 6–21 times lower than those in the grate combustion of wood residues. Grate combustion of pellets and gasification combustion of wood residues generated 1.3–6.6 times higher PM1 than HFO. The particle number emissions were around 2×10^{13} particles/MJ and were similar to those of biomass combustion without effective filtration. The wood combustion plants operating with electrostatic precipitators had PM1 emissions similar to those of HFO boilers but clearly lower particle number emissions. The wood combustion particles were formed mainly of alkali metals salts and smaller amounts of Zn, OC and EC, while the fine particles from the HFO boiler were formed of several transition metal compounds, sulphuric acid, EC and OC. In addition, HFO combustion generated high SO_2 gas emissions that participate in the formation of secondary aerosol particles in the atmosphere. Thus,

in the small district heating-scale, replacing oil-fired boilers can significantly increase primary PM1 emissions if no effective flue gas cleaning systems or more advanced combustion technologies are applied. However, the health and climate effects of the emissions originating from biomass and heavy fuel oil combustion may differ significantly due to the very different chemical and physical properties of the emissions.

5 AUTHOR'S CONTRIBUTION

Papers I and II describe studies from district heating boilers. They were carried out in cooperation between the VTT Technical Research Centre of Finland and the University of Kuopio, under the supervision of J. Jokiniemi. H. Puustinen from VTT was responsible for arranging the combustion experiments. The author was responsible for the data interpretation, model calculations and manuscript writing. The experiments and experimental data analysis were carried out by H. Puustinen and J. Hokkinen from the VTT and P. Yli-Pirilä and the author from the University of Kuopio. In addition, technical personnel from VTT, Nab-Labs Process Analytics and the heating plants participated in the experiments. P. Willman from the University of Kuopio carried out the thermal optical carbon analysis runs.

Paper III describes laboratory experiments with a pellet stove operated with different fuels. The author carried out the major work regarding the experiments, data processing and interpretation, modeling and manuscript writing, under the supervision of T. Raunemaa and J. Jokiniemi. K. Hytönen performed the VOC analyses and the data analysis, and the manuscript writing related to the VOC results. The combustion experiments were arranged together with J. Tissari. P. Willman carried out the thermal optical carbon analysis runs.

Paper IV describes experiments with a laminar flow reactor in the laboratory. The author was responsible for constructing the experimental setup, measurements, data analysis, modeling and manuscript writing, under the supervision of J. Jokiniemi. T. Lind participated in the planning of the experiments and manuscript writing.

In **Paper V**, the combustion experiments with agricultural fuels in the laboratory of TTS Research, Rajamäki, Finland, are analysed. The experiments were arranged mainly by J. Kouki and K. Vuorio from TTS Research. The author carried out the measurements together with J. Tissari and participated in the data interpretation and manuscript writing, especially regarding the ash behavior of different fuels. J. Tissari was responsible for writing the manuscript. The work was supervised by J. Jokiniemi. P. Willman carried out the thermal optical carbon analysis runs.

Paper VI is a conference article reviewing the outcomes from several combustion experiments in the field. Most of the data originates from the combustion experiments organized by Vapo. The author was responsible for the measurements, data analysis, modeling and manuscript writing, under the supervision of J. Jokiniemi. H. Lamberg contributed to the measurements, data analysis and interpretation of the results. P. Willman carried out the thermal optical carbon analysis runs.

6 CONCLUSIONS

In this work a set of experiments were carried out to study fine particle emissions, their formation and ash behavior. The experimental work included combustion studies with a number of Finnish biomass fuels in several small- to medium-scale combustion units and in a laboratory-scale flow reactor. The quantities, chemical compositions and physical properties of the fine particles were characterized in detail, applying several measurement and analysis techniques. In addition, flue gas compositions and coarse fly ashes were measured and chemical characterizations of the fuels were carried out.

With wood fuels consisting mainly of stem material, the amounts of fine particles generated were in the range of 13–92 mg/MJ (as PM1) and $1\text{--}5 \times 10^{13}$ particles/MJ, when measured after heat exchangers. The number-based geometrical mean diameter of the particles varied between 60 and 150 nm in aerodynamic diameter. Significant fractions of particle emissions were formed from ultra-fine particles ($d_p < 100$ nm). The fine particles observed with electron microscopy were mainly single spherical primary particles or compact agglomerates formed of a few primary particles. The fine particles were composed mainly of ash material, in which the most abundant species were K, Cl, SO_4 , Zn, Na and CO_3 . The fractions of soot (elemental carbon) and organic carbon, formed due to incomplete combustion, ranged between 0 and 22 % of the total PM1.

Bark material generated clearly higher fine particle emissions than stem materials, and the addition of bark to a fuel mixture considerably increased fine particle formation. This was because of the higher ash contents and especially the higher potassium contents in the bark fuels. In some appliances, high ash contents also increased the formation of soot and organic material due to impaired combustion conditions. In contrast, the addition of peat to wood combustion decreased PM1 emissions, due to the decreased release of alkali metals into the fine particle fraction. The cereal fuels (rape seed, rape seed residue, oat) had fine particle emissions comparable to those of stem wood fuels, despite the very high ash and alkali metal contents. The chemical composition of fine particles differed from that of wood by high fractions of phosphate. When comparing the emissions, it should be noted that peat and cereals have significantly higher emissions of SO_2 and NO_x gases, which are important pollutants and participate in the secondary particle formation in the atmosphere.

The main factor influencing fine particle formation was the release of alkali metal vapours from the fuel. The observed release fractions were highest for stem-rich wood materials and lowest for peat and cereal fuels. Silicates in the fuel were found to decrease the alkali release and increase the retention of alkali metals in the bottom ash fraction, probably due to the formation of alkali silicate compounds. Chlorine in the fuel was found to increase the alkali release, probably due to the increase in the formation of alkali chloride vapours that vaporize easily. Sulphur in the fuel was found to decrease the effects of chlorine by a sulphation reaction. Correlations between

S/Cl ratios and alkali release fractions were observed. The release of zinc was relatively high with all fuels and it was generally less influenced by the fuel properties than alkali metals. However, chlorine was found to have effects on zinc release.

According to the measured flue gas and fine fly ash compositions and thermodynamic equilibrium calculation results, the first fine fly ash particles can be formed by the oxidation of Zn vapour to ZnO. This is followed by the formation of alkali sulphates. The remaining alkali vapours may condense as chlorides and hydroxides or form carbonates and nitrates. With phosphorus-rich annual biomasses, alkali phosphates are likely to be formed.

In general, biomass combustion was found to generate high fine particle emissions, when compared with fossil oils, for example. Fine particle formation and chemical composition was found to be significantly influenced by fuel properties. As small-scale combustion units often are not equipped with flue gas cleaning technology, the choice of fuel has an important effect on fine particle emissions and their potential effects in the environment. In addition, the fuel has important effects on the operation and efficiency of the boilers in both small- and large-scale. The release and chemical reactions of ash species in the boiler determine the quantity and chemical composition of the fine fly ash fraction formed in the boiler. Furthermore, combustion conditions determine the soot and organic material fractions released from the combustion process. The emissions can be decreased by flue gas cleaning systems, modifying the fuel feedstock by different fuel blends or additives and by developing combustion technologies.

Replacing small heavy fuel oil fired boilers with biomass-fired boilers may significantly increase fine particle emissions on a mass basis if no effective flue gas cleaning systems are used. The chemical and physical properties of fine particles and the quantities of gaseous emissions vary considerably between biomass and heavy fuel oil boilers, and therefore they are likely to have very different effects on health and the environment.

In the future, more information is needed on the role of fine particle chemical composition and physical structure on adverse health effects and climate effects. This would help in applying appropriate measures and methods for decreasing the harmful effects of fine particle emissions. Understanding the role of fuel ash composition in the release of ash species would help in finding optimal fuel mixtures. Moreover, additive-based methods and advanced air staging in the boiler can be used to decrease ash release and modify ash reactions. These methods may offer an economically feasible way to decrease both fouling problems and emissions. From a theoretical point of view, the chemistry behind fly ash formation in biomass combustion is still not fully understood. First, the release of fine fly ash-forming elements is poorly understood, and cannot be predicted based on fuel composition analyses. Second, the sulphation of alkali metals cannot be correctly predicted in real world combustion conditions. Third, better understanding of the behavior of zinc and other volatile metals is needed for building mechanistic models for fine fly ash formation. Fourth, the role of phosphorus in the chemistry of fine fly ash formation with annual plant biomasses is unclear.

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APPENDIX I: Fuel properties^a

Fuel	Paper	H ₂ O	Ash	HHV	N
		m%	m%	MJ/kg	m%
Oat	V	11.4	2.39	19.6	na
Wood-pellet	V	5.3	0.28	20.2	na
Rape seed	V	5.5	4.42	27.1	na
Rape seed-residue	V	6.8	6.08	24.2	na
Oat-Peat (80/20%)	V	11.2	2.4	19.7	na
Oat + 5% Kaolin	V	≈10.8	≈7.3	≈18.6	na
Wood + 1% Kaolin	V	≈5.2	≈1.3	≈19.9	na
Pellet (Commercial)	III	5.9	0.3	20.3	na
Pellet (Birch bark)	III	6.1	1.5	26.0	na
Pellet (Birch stem)	III	7.0	0.4	19.5	na
Pellet (Spruce bark)	III	6.8	4	20.8	na
Pellet (Spruce stem)	III	5.8	0.5	20.3	na
Pellet (Alder bark)	III	5.4	3	22.5	na
Pellet (Alder stem)	III	3.4	0.5	20.2	na
Pellet (Pine bark)	III	6.9	1.6	21.0	na
Pellet (Pine stem)	III	5.8	0.4	20.4	na
Pellet (Willow bark)	III	6.7	3.9	20.6	na
Pellet (Willow stem)	III	7.5	0.6	19.6	na
Sawdust & bark (Plant A)	I,II,VI	51.0	0.93	20.5	0.3
Forest residue (Plant D)	I,II,VI	47.0	na	20.5	na
Sawdust & bark (Plant C)	I,II,VI	50.0	1.7	20.6	0.2
Pellet (stem 1)	VI	8.3	0.3	20.3	0.16
Pellet (bark)	VI	10.0	2.7	20.7	0.23
Pellet mix (stem 1 & bark)	VI	9.2	1.3	20.5	0.19
Pellet mix (peat & bark)	VI	14.7	3.8	21.3	0.77
Pellet mix (stem+bark & peat)	VI	12.3	3.1	21.1	0.6
Pellet (stem + bark)	VI	8.3	1.6	20.5	0.18
Pellet (Peat)	VI	18.2	5.3	21.9	1.43
Pellet (stem 2)	VI	7.7	0.3	20.4	0.16
Pellet mix (stem 2 & peat)	VI	12.5	2.6	21.1	0.66

^aConcentrations are given as mass percent of dry fuel except moisture which is mass percent of wet fuel.

na = not analysed

APPENDIX II: Ash-forming elements in fuels^a

Fuel	Paper	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	(K+Na)/(Cl+2S)*
Oat	V	24	640	80	5290	1330	40	43	4020	1640	na	28	578	3.27
Wood-pellet	V	10	940	10	670	200	70	10	40	70	na	7	42	7.75
Rape seed	V	ud	5410	60	7910	3380	20	25	8880	4350	na	34	117	2.86
Rape seed-residue	V	9	5980	90	10170	5410	50	36	12640	4910	na	58	92	3.31
Oat-Peat (80/20%)	V	176	836	422	4270	1190	40	50	3278	1544	na	25	518	2.88
Oat + 5% Kaolin	V	10474	608	76	5026	1264	38	41	3819	1558	na	27	549	3.27
Wood + 1% Kaolin	V	2100	931	10	663	198	69	10	40	69	na	7	41	7.75
Pellet (Commercial)	III	na	752	na	409	164	na	na	49	53	na	9	41	5.27
Pellet (Birch bark)	III	na	3900	na	1250	426	na	20	459	342	na	127	300	2.38
Pellet (Birch stem)	III	na	758	na	626	171	na	112	110	82	na	18	199	3.03
Pellet (Spruce bark)	III	na	13500	na	2025	704	na	9	463	393	na	143	213	4.30
Pellet (Spruce stem)	III	na	829	na	606	228	na	na	170	117	na	12	29	5.90
Pellet (Alder bark)	III	na	7590	na	2695	582	na	na	577	567	na	103	98	5.95
Pellet (Alder stem)	III	na	1115	na	986	208	na	na	165	167	na	25	41	6.72
Pellet (Pine bark)	III	na	4340	na	1580	464	na	8	375	309	na	26	83	5.70
Pellet (Pine stem)	III	na	792	na	661	267	na	na	232	135	na	10	51	4.79
Pellet (Willow bark)	III	na	11700	na	3875	727	na	77	1200	891	na	211	82	6.32
Pellet (Willow stem)	III	na	1110	na	1245	183	na	44	396	169	na	17	43	8.76
Sawdust & bark (Plant A)	I,II,VI	89	2900	67	1070	400	170	24	245	190	78	42	80	5.44
Forest residue (Plant D)	I,II,VI	170	1740	454	1470	357	141	26	169	128	185	23	1520	0.86
Sawdust & bark (Plant C)	I,II,VI	na	na	na	na	na	267	na	na	100	na	63	118	-
Pellet (stem 1)	VI	9	766	46	490	148	68	<25	110	ud	700	9	280	-
Pellet (bark)	VI	455	4830	1500	1600	403	142	280	390	200	2300	25	120	8.17
Pellet mix (stem 1 & bark)	VI	232	2798	490	1100	276	105	160	260	ud	2500	17	250	4.98
Pellet mix (peat & bark)	VI	1325	4146	4100	1200	527	120	610	500	900	5000	17	290	2.58
Pellet mix (stem+bark & peat)	VI	1162	2352	3300	850	425	86	510	380	700	5400	10	220	2.57
Pellet (stem + bark)	VI	184	1840	760	1000	234	85	220	210	ud	2400	13	110	11.33
pellet (Peat)	VI	2630	3120	7400	790	712	88	1100	630	1600	7800	5	520	1.72
Pellet (stem 2)	VI	19	645	52	470	149	60	250	130	ud	<150	8	220	3.69
Pellet mix (stem 2 & peat)	VI	1063	1635	3500	560	374	71	570	360	700	3700	7	310	1.99
Wood dust	IV	9	1280	25	475	228	73	214	90	73	na	29	99	5.43
Wood dust & HCl	IV	10	1280	25	475	228	73	214	90	73	na	29	935	0.78
Wood dust & HCl + SO ₂	IV	11	1280	25	475	228	73	214	90	4211	na	29	928	0.23
Wood dust & SO ₂	IV	12	1280	25	475	228	73	214	90	5831	na	29	99	0.23

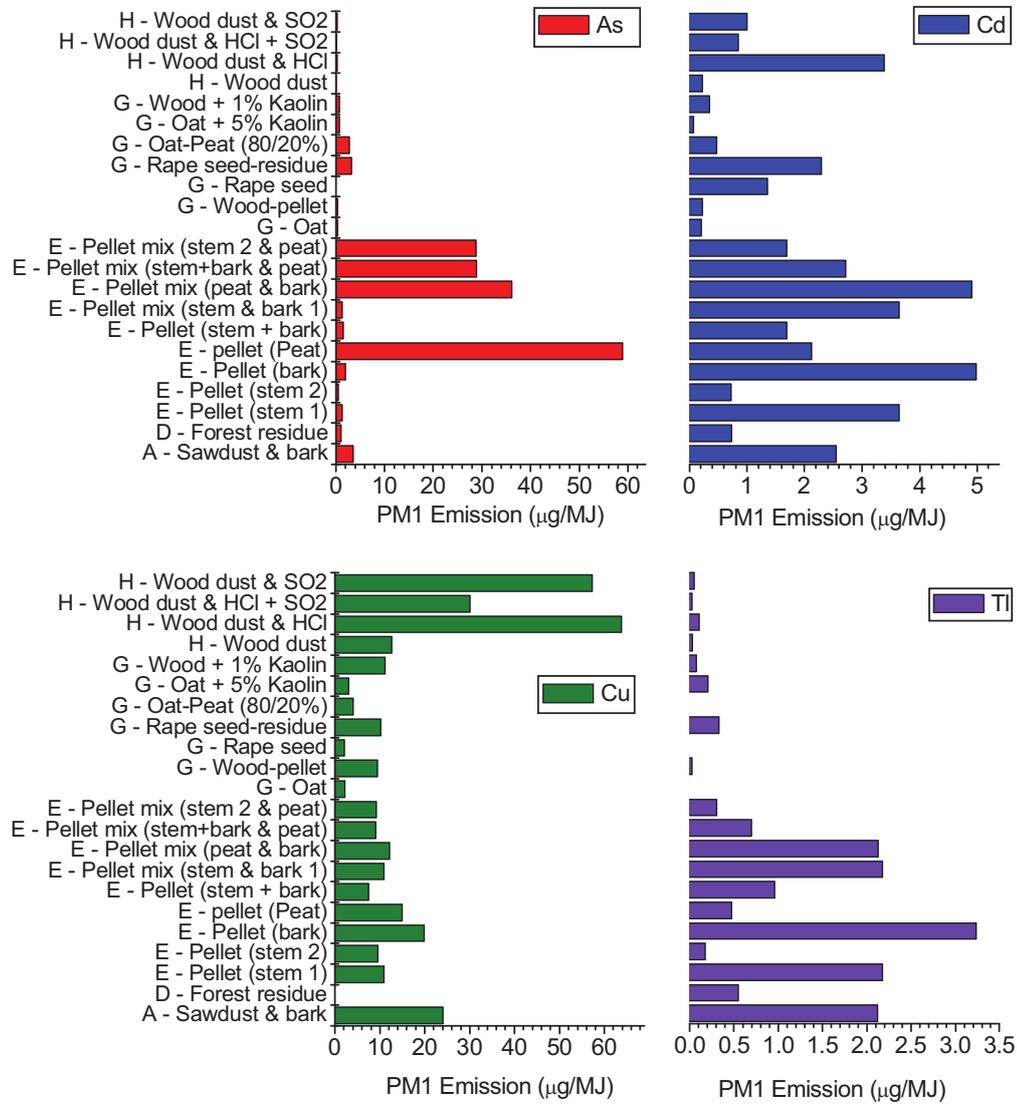
^aConcentrations of elements given as mg/kg dry fuel.

*molar ratio in fuel

na = not analysed

ud = under detection limit

APPENDIX III: Trace metals in PM1 fraction



APPENDIX III: Trace metals in PM1 fraction (cont.)

