SMALL-SCALE PELLET BOILER EMISSIONS – CHARACTERIZATION AND COMPARISON TO OTHER COMBUSTION UNITS

HEIKKI LAMBERG

Department of Environmental Science
Faculty of Science and Forestry
University of Eastern Finland
Kuopio, Finland

Academic Dissertation

To be presented, with permission of the Faculty of Science and Forestry of the University of Eastern Finland, for public examination in Auditorium TTA, Tietoteknia Building at the University of Eastern Finland, Kuopio, on 21st November, 2014, at noon.

Kuopio 2014

Author's address: Fine Particle and Aerosol Technology Laboratory
                     University of Eastern Finland
                     Department of Environmental Science
                     P.O.Box 1627
                     70211 Kuopio
                     Finland

Heikki Olavi Lamberg,
University of Eastern Finland, 2014

ABSTRACT

Residential combustion has been identified as one of the main sources of particulate matter (PM); fine particles are important because of their adverse effects on human health and the environment. In this thesis, fine particle emissions originating from residential pellet combustion were characterized in different operational situations and using different raw materials as pellet fuel. Moreover, pellet combustion emissions were compared with those from other combustion technologies used for heat production, including batch-wise operated wood stoves, residential-scale oil boilers and medium-scale plants utilizing wood chips and heavy fuel oil.

Particle emissions from pellet combustion in modern pellet boilers are low compared to those of other wood-fueled residential appliances; these particles primarily consist of fine inorganic fly ash. Decreasing air-to-fuel ratio of primary combustion while increasing air-to-fuel ratio of secondary combustion affected the release of fine fly ash without deteriorating the combustion conditions, resulting in significant reductions in fine particle emissions. In low-load conditions, the amount of fine fly ash particles remained constant, but fine particle emissions increased due to soot formation.

The pellet raw material largely affected fuel originated fine fly ash emissions, whereas emissions of incomplete combustion remained low. The addition of peat to biomass fuels was found to decrease fine particle emissions due to the increased binding of alkali metals in the bottom ash. The use of bark or straw pellets resulted in elevated fine fly ash particle emissions because of the larger alkali metal contents in the fuel. Thus, only stem-wood-based pellets should be used in current residential-scale combustion technology to prevent additional particle emissions.

Combustion technology had a substantial effect on particle and gaseous emissions in the studied batch-wise operated appliances, although the emissions are generally higher than from pellet combustion. In batch combustion, fine particles are mainly formed of elemental carbon and organic matter, although fine fly ash is also present in these particles. Based on the analyzed particle components, polycyclic aromatic hydrocarbons (PAHs) were found to be the most sensitive compound for combustion quality, indicating that the harmfulness of PM from different sources may vary more than what is estimated for particle mass emissions alone.

Although particle emissions from light fuel oil combustion are low, this combustion produces more PAHs than pellet combustion. Heavy fuel oil exhibited similar PM emissions as pellet boilers; however, significantly more PAHs and heavy metals were also produced.

There are numerous options for reducing emissions using combustion technology and flue-gas cleaning. Overall, combustion technology provides the possibility of decreasing emissions from residential combustion; however, firmer emission regulations are needed to increase the utilization of low-emission technologies.

Keywords: aerosol, air pollutions, agricultural fuel, biomass, boiler, emission characterization, fine particle emissions, masonry heater, particulate matter, peat, pellets, residential combustion, small-scale combustion

Acknowledgements

I would like to express my gratitude to my principal supervisor Professor Jorma Jokiniemi for guidance and providing interesting and challenging research topics throughout the years. I am thankful to my supervisors Olli Sippula (Ph.D) and Jarkko Tissari (Ph.D.). Your help and support in every step of this work has been enormous. I am also very grateful to the Head of the Department of Environmental Science, Professor Maija-Riitta Hirvonen, and her group for the cooperation in the studies dealing with particle toxicological effects.

I want to thank the official reviewers of my thesis Professor Veli-Matti Kerminen and Senior Researcher Patrik Yrjäs (Ph.D.) for reviewing my thesis and giving valuable comments on it. I am grateful to Professor Ralf Zimmermann for kindly accepting the invitation to be the official opponent during the public examination of the thesis.

A valuable part of this work was made by the co-authors of the four papers. I gratefully thank all of them for their contribution. I am thankful to all of my present and past colleagues at the Fine Particle and Aerosol Technology Laboratory. Coffee breaks, lunches and all the other scientific and non-scientific discussions have been something to wait for when the office work has tasted like a two-hour-old chewing gum. I have met many interesting people during this work at different occasions. These people have made my work more interesting than I could have imagined.

I want to thank my friends who have been around for all of these years. I am especially grateful to my family for all the support throughout the years. Kiitos!

Kuopio, October 2014

Heikki Lamberg

Abbreviations

CMH=conventional masonry heater
CO_3=carbonate carbon
DGI=Dekati Gravimetric Impactor
DLPI=Dekati Low-Pressure Impactor
DR=dilution ratio
EC=elemental carbon (soot)
ED=ejector diluter
ELPI=Electrical Low-Pressure Impactor
ESP=electrostatic precipitator
FMPS=Fast Mobility Particle Sizer Spectrometer
GC-MS=Gas Chromatography Mass Spectrometry
HFO=heavy fuel oil
ICP-AES=Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS=Inductively Coupled Plasma Mass Spectrometry
ISO=International Organization for Standardization
LFO=light fuel oil
MMH=modern masonry heater
NO_x=nitrogen oxides
OC=organic carbon
OGC=organic gaseous compounds
OM=organic matter
PAH=polycyclic aromatic hydrocarbons
PB=pellet boiler
PCDD/F=polychlorinated dibentzodioxins/furans
PM_1 ($PM_{2.5}$, PM_{10})=Mass of particles below aerodynamic diameter of 1 μm (2.5 μm, 10 μm)
POM=particulate organic matter
PRD=porous tube diluter
SOA=secondary organic aerosol
SO_x=sulfur oxides
SS=sauna stove
VOC=volatile organic compounds
λ=air-to-fuel ratio

List of publications

This thesis is based on four publications that are referred to in the text using Roman numerals (i.e., I-IV). The publications are reproduced with the kind permission of the respective journals.

Paper I   Lamberg, H., Sippula, O., Tissari, J., Jokiniemi, J. (2011). Effects of Air Staging and Load on Fine-Particle and Gaseous Emissions from a Small-Scale Pellet Boiler. *Energy & Fuels* 25, 4952–4960.

Paper II   Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.-R., Jokiniemi, J. (2011). Physicochemical characterization of fine particles from small-scale wood combustion. *Atmospheric Environment* 45, 7635–7643.

Paper III   Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O. (2013). Fine Particle and Gaseous Emissions from a Small-Scale Boiler Fueled by Pellets of Various Raw Materials. *Energy & Fuels* 27, 7044–7053.

Paper IV   Kaivosoja, T., Jalava, P.I., Lamberg, H., Virén, A., Tapanainen, M., Torvela, T., Tapper, U., Sippula, O., Tissari, J., Hillamo, R., Hirvonen, M.-R., Jokiniemi, J. (2013). Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20–25 kW) and medium (5–10 MW) scale. *Atmospheric Environment* 77, 193–201.

Contents

1 INTRODUCTION

Particulate matter (PM) is defined as the total mass of suspended particles in the air. PM is typically divided into three subclasses, i.e., PM_{10}, $PM_{2.5}$ and $PM_{0.1}$, which are defined as particle matter with an aerodynamic diameter smaller than 10 µm, 2.5 µm and 0.1 µm, respectively. $PM_{2.5}$ particles are generally called "fine particles"; however, this term can also be applied to the number or surface area based on particle diameters less than 2.5 µm. In the atmosphere, particles can be solid or liquid; the mixture of particles and gases is called "aerosol".

Fine particles originate from natural and anthropogenic sources. Examples of natural sources include volcanoes, natural forest fires, biogenic aerosols, windborne dust and sea spray (Andreae and Crutzen 1997, Seinfeld and Pandis 1998). The most important sources of anthropogenic particles are different types of combustion processes, such as domestic heating, power plants and internal combustion engines. When particles from combustion sources are discussed, particles with aerodynamic diameters less than 1 µm or 2.5 µm (PM_1 or $PM_{2.5}$) are often used, whereas particles with sizes ranging from 2.5 µm to 10 µm are called coarse particles. Examples of coarse particle sources include road wear and wind-blown dust. On the contrary to primary particles, which are directly emitted from various sources in particulate form, secondary particles are formed in the atmosphere through gas-to-particle conversion processes. The most common types of secondary aerosol formation are sulfur dioxide (SO_2) and nitrogen oxide (NO_x) reactions in the atmosphere and the oxidation of organic gases. The products of the latter mechanism are generally referred to as secondary organic aerosols (SOAs). Primary and secondary particles form the total particulate matter in the atmosphere. These particles constantly interact with their surroundings.

Fine particles are known to have adverse effects on human health and to cause respiratory and cardiac symptoms and even premature death, especially among those with reduced health conditions, e.g., children, elderly and those with chronic diseases (Dockery and Pope 1994, Pope et al. 2002). Recently, the IARC has classified outdoor air pollution and particulate matter from outdoor air as being carcinogenic to humans (Loomis et al. 2013). Due

to their small sizes, fine particles can penetrate deep into the lungs and enter the blood. Thus, health-related problems are the primary concern for fine particles, requiring emission regulation. The physical and chemical properties of these particles greatly affect their health effects. Combustion sources are highly heterogenic emission sources; the characteristics of particles and gases vary substantially from one source to another (Flagan and Seinfeld 1988, Ostro et al. 2007). Furthermore, fine particles also cause environmental problems that affect solar radiative forcing, corrode materials and cause impaired visibility (Horvath 1993, Kucera et al. 1995).

Wood is the most commonly used biomass fuel in Nordic countries due to the large forest base, forest industry and relatively easy access to cheap wood for many individuals. Based on the total heat and power production in Finland in 2013, 24% was produced using wood biomass, primarily from by-products of the forest industry (Statistics Finland, 2014), and 4.3% (2011) of the total energy was produced with wood in households (Statistics Finland 2012). Although wood combustion produces less carbon dioxide (CO_2) emissions than fossil fuel combustion and residential wood combustion has a great potential for increasing biomass usage, there is the risk of increased emissions of particles and gases and detrimental air quality effects. Typically, emissions from large-scale heat and power production units are low due to legislative measures, well-controlled combustion processes and flue-gas after-treatment techniques (Sippula 2010). However, emissions from smaller units are often not well controlled, which is due to the use of old appliances, conventional and cheap technology, unoptimized use of appliances and a wide variety of used fuels (Tissari 2008). Residential appliances do not typically have emission limits, which is still the case in many countries. Although there are new, less-polluting appliances that are available, old appliances will remain in use for a long time.

Residential wood combustion is known to be a significant source of particulate matter (McDonald et al. 2000, Johansson et al. 2004, Tissari et al. 2007, Karvosenoja et al. 2008, Brandt et al. 2011, Saarnio et al. 2012) and organic compounds, including polycyclic aromatic hydrocarbons (PAHs) (Schnelle-Kreis et al. 2007, Bari et al. 2011, Elsasser et al. 2012, Crippa et al. 2013). The proportion of PM originating from wood combustion sources has been reported to vary greatly in different locations, for example, 3% in Mediterranean urban background air (Reche et al. 2012), 14% in Central Europe urban background air (Brandt et al. 2011), and up to 66% in Finnish

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suburban air in winter (Saarnio et al. 2012). Certain types of combustion appliances have been identified to contribute greatly to the total emissions from residential wood combustion (Meyer 2012).

Wood pellets are primarily used in continuously operated combustion appliances. These pellets are generally made of sawdust, cutter chips or other wood industry residues. Pellets have low moisture contents, high energy densities, homogenous sizes and low ash contents. Due to their homogenous features, pellets (when used as fuel) have enabled the development of fully automatic residential-scale combustion systems; the ease of use is essential for these systems. Additionally, pellets can be used in industrial power plants designed for pulverized fuels (Obernberger and Thek 2010). Pellets can also be manufactured from non-traditional raw materials, such as bark, straw, reed canary grass or logging residues, and different raw materials can be mixed to form homogenous pellets. Fine particle emissions from modern pellet appliances are typically fuel derived and contain fine fly ash (Wiinikka et al. 2007, Tissari et al. 2008a, Verma et al. 2011, Schmidl et al. 2011), whereas PM emissions from poor combustion conditions can be almost entirely products of incomplete combustion (Tissari et al. 2008b, Elsasser et al. 2013).

The use of wood in heat and power production is increasing. Part of this increased use will be due to the increase in residential appliances. Thus, it is important to ensure that the change from fossil fuels to renewable fuels, which is a part of the climate policy, will be performed without additional air pollution problems and excess stress on both human health and the environment.

2 AIMS OF THIS STUDY

The focus of the research presented in this thesis was the physical and chemical characterization of fine particle emissions produced via pellet combustion. Furthermore, emissions were compared with various small- and medium-scale residential combustion appliances. The individual studies can be summarized as follows.

- Paper I analyzed pellet boiler emissions in different operational situations, including different combustion air settings.
- Paper II characterized emissions from continuous combustion and batch combustion for different combustion technologies.
- Paper III analyzed the effects of pellet fuel raw materials on PM emissions.
- Paper IV compared PM emissions from pellet combustion with those from light fuel oil combustion (small scale) and with the emissions from heating plants fired using wood chips and heavy fuel oil (medium scale).

Furthermore, the PM samples characterized in Papers II and IV were used in toxicological studies by Tapanainen et al. (2011, 2012) and Kasurinen et al. (2014). However, the results of these studies are not discussed in this thesis.

3 SCIENTIFIC BACKGROUND

3.1 Fuels

The main components of biomass fuels are carbon (C) (50%), oxygen (O) (42%) and hydrogen (H) (6%). The amount of volatile matter is typically between 70–86 w-% (d.b.) (van Loo and Koppejan, 2008), which is substantially higher than coal (approximately 30–40 w-%) (Vassilev and Vassileva 2009). Freshly cut wood has a high moisture content and must be dried before use. In power plants, the moisture content of wood chips can be up to 50% (Kaivosoja et al. 2013), whereas the moisture content of wood pellets is typically less than 10% (van Loo and Koppejan, 2008). Log woods are most commonly used in households; these woods are not easily used in automatic systems. Compared with pellets, log woods require more storage space and labor for moving from storage to the heating system. Wood chips, which are often used in farms, can be used in automated systems. However, due to their low density, wood chips require plenty of storage space. Other biomass products are also used as energy sources.

3.1.1 Pellet fuels

The pellet manufacturing process includes the following steps. 1) The raw material is dried. 2) The material is milled to reduce the particle size and to homogenize the material. 3) The particles are conditioned via the addition of steam to cover the particles with a thin liquid layer; this process reduces adhesion. 4) The raw material is formed into pellets by being pressed through a die. 5) The pellets are cooled because their temperature increases during the pelletizing process. The diameter of the pellets is typically 6-12 mm (van Loo and Koppejan, 2008) (Figure 1). Classification systems have been created for pellet fuels to ensure the proper quality of pellets that are used in different units. The ENPlus certification, which is applied in many parts of Europe, divides pellets into three different classes according to threshold values for the pellet diameter, length and contents of moisture, ash, nitrogen (N), sulfur

(S) and chlorine (Cl) in the fuel (Table 1) (European Pellet Council 2013). ENPlus also sets requirements for the raw materials that are used in the three different pellet quality classes.

Figure 1. Examples of pellets made from different raw materials: a) commercial wood pellet, b) peat pellet, c) a mixture of pine bark and peat and d) rye straw pellet.

3.2 Combustion

In the ideal combustion of hydrocarbons, carbon (C) and hydrogen (H) react with oxygen (O_2) to generate heat and form both CO_2 and water (H_2O). In real applications, combustion conditions are never ideal. Moreover, fuel and combustion air contain several components that affect the combustion process and emission formation. The combustion of solid fuel in real-life applications always require more air than what is theoretically needed; therefore, the general air-to-fuel ratio (lambda, λ) exceeds 1. In addition, the air-to-fuel ratio varies in different areas of the combustion chamber. Optimal λ values also vary between different combustion appliance types, unit sizes and fuels. For example, in spark-ignited internal combustion engines, λ can be less than 1 (Flagan and Seinfeld 1988). Moreover, in biomass-fired industrial-scale units (rotating grate), λ is approximately 1.3 (5% excess oxygen, O_2) (Sippula et al. 2009a), and in small-scale pellet boilers, λ is approximately 2 (10% O_2) (Tissari et al. 2008a).

Table 1. ENPlus requirements for pellets used for heating purposes (Modified from European Pellet Council 2013).

	Unit	ENplus-A1	ENPlus-A2	EN-B
Diameter	mm	6 or 8	6 or 8	6 or 8
Length	mm	$3.15 \leq L \leq 40$	$3.15 \leq L \leq 40$	$3.15 \leq L \leq 40$
Moisture content	w-%	≤ 10	≤ 10	≤ 10
Ash content	w-%	≤ 0.7	≤ 1.5	≤ 3.0
Mechanical durability	w-%	≥ 97.5	≥ 97.5	≥ 96.5
Fines (<3.15 mm)	w-%	< 1	< 1	< 1
Lower heating value	MJ/kg	$16.5 \leq Q \leq 19$	$16.3 \leq Q \leq 19$	$16 \leq Q \leq 19$
Bulk density	kg/m^3	≥ 600	≥ 600	≥ 600
N content	w-%	≤ 0.3	≤ 0.5	≤ 1.0
S content	w-%	≤ 0.03	≤ 0.03	≤ 0.04
Cl content	w-%	≤ 0.02	≤ 0.02	≤ 0.03
Ash melting behavior	°C	≥ 1200	≥ 1100	≥ 1100
Wood types permitted to be used for wood pellet production		Stem wood and chemically untreated residues from the wood processing industry	Whole trees w/o roots, stem wood, logging residues, bark, and chemically untreated residues from the wood processing industry	Forest, plantation and other virgin wood, chemically untreated residues from the wood processing industry, and chemically untreated used wood

3.2.1 Combustion units

Combustion technologies vary widely based on the different size classes and fuels. Fuels used in heat and power production are generally either solid, gas or liquid. Solid fuel combustion technologies include fixed bed, fluidized bed and pulverized fuel combustion with different variations for specific applications. Fixed bed combustion is often used in residential-scale solid fuel combustion. On the contrary, the combustion of liquid fuels is performed in burners in which the fuel is first sprayed before the combustion.

Combustion processes are well-controlled in large power plants. The processes are optimized for certain types of fuels. Moreover, flue-gas cleaning technologies are commonly used, such as electrostatic precipitators (ESP), to ensure good combustion quality and low emissions. The state-of-the-art combustion technology that is used in residential appliances contains many of the same control techniques that are used in large units. Such appliances can be fueled by pellets, wood chips or wood logs, and the combustion units include automated fuel feeding and automatically controlled air input. With proper control and design and good quality fuel, emissions from residential wood combustion can be low (Wiinikka et al. 2004, Sippula et al. 2007, Tissari et al. 2008a). The present situation of residential combustion in Europe is unfortunately bleak. There are numerous residential appliances with either poor or lacking combustion controls. Moreover, the quality of fuel used in these appliances is typically bad, and the appliance operations are far from optimal.

3.2.2 Continuous pellet combustion

Residential-scale combustion appliances that use solid fuel can be divided into two main categories: batch combustion appliances and continuously fired appliances. Combustion processes in appliances equipped with continuous combustion are generally more precisely controlled than batch combustion appliances. Pellets and wood chips are the most commonly used fuels in continuous combustion appliances in the Nordic countries, whereas wood logs are most often used as fuels in batch combustion appliances.

In pellet appliances, fuel is continuously inserted by feeding from the side, bottom or top, determined by the burner technology (Figure 2). Due to the

continuous behavior of the process, which is ensured with logic-controlled fuel and air feeds, both heat release and emission formation are more stable than in batch combustion (van Loo and Koppejan, 2008). To ensure proper combustion conditions, different sensor technologies, such as lambda (λ), carbon monoxide (CO), and temperature controls, can be used for controlling the combustion conditions and adjusting the air and fuel feeds. In pellet stoves, heat is typically transported to the air around the stove via convection, but in pellet boilers, heat is accumulated and transferred to circulated water via a heat exchanger. Modern pellet boilers are nearly as ease to use as oil and gas boilers, which has made pellet systems more attractive for residential use. Oil boiler systems can also be retrofitted to be fueled with pellets by replacing the burner and fuel conveyor system.
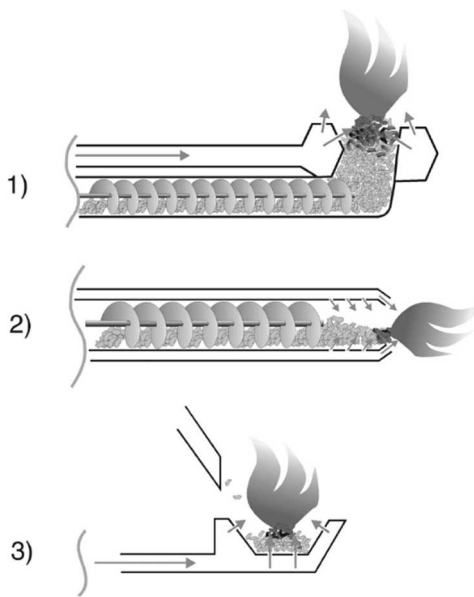

Figure 2. Examples of the most commonly used wood pellet feeding techniques in residential appliances (van Loo and Koppejan, 2008): (1) underfed burner, (2) horizontally fed burner and (3) overfed burner.

3.2.3 Batch combustion

Batch combustion appliances are the most common residential appliances. In batch combustion, a batch of wood is inserted into the appliance and fired. After a certain period of time, typically when the flames burn down, the next batch is added to the appliance. This activity is repeated for a certain period of time, which is based on the appliance type and the required amount of heat. Due to the periodic behavior of the combustion process, heat release and the formation of emissions are not stable. In uncontrolled systems, an addition of a new batch of wood can result in fast pyrolysis of the fuel and in inadequate mixing of gases and oxygen, which leads to incomplete combustion and high emissions (Tissari et al. 2009). Because the behavior of combustion in batch combustion appliances varies significantly with time, designing a properly working appliance can be challenging. In modern batch combustion appliances, the combustion rate is regulated by reducing the amount of combustion air that enters through a grate; a portion of the air is transferred into the upper zone of the combustion chamber as secondary air (Nuutinen et al. 2014). This technique reduces the variations in the batch combustion process.

3.3 Emissions

The emissions from biomass combustion can be divided into two main classes: gaseous and particulate emissions. Particle emissions can be further divided into three main subclasses: organic material, soot and inorganic material. Particulate organic matter (POM) and soot are products of incomplete combustion; their contributions to the total PM emissions can vary significantly depending on the combustion conditions. Inorganic fine fly ash particles are fuel derived. Moreover, because these particles are not products of incomplete combustion, their reduction is not possible by improving combustion efficiency.

3.3.1 Soot

Soot is one of the most important pollutants originating from combustion processes due to its effects on both climate and health. The International Agency for Research on Cancer has recently classified diesel soot as being carcinogenic to humans (IARC 2012). Soot has adverse effects on visibility (Horvath 1993) and is known to be a carrier for PAH species (Richter and Howard 2000, Oster et al. 2011, Laskin et al. 2012, Furuhata et al. 2012). Recent findings regarding the climate effects of soot have highlighted the significance of soot emissions and emission controls (Jakobson 2010, Bond et al. 2013), especially in the Arctic (Stohl et al. 2013). The formation of soot creates the characteristic yellow light in candles; moreover, soot is necessary in boiler flames to obtain good radiative heat transfer (Flagan and Seinfeld, 1998).

Different definitions and terminology are used in the characterization of soot (Petzold et al. 2013). The so-called thermal-optical method is often used in combustion studies to determine the fractions of soot and organic carbon (OC). In this context, soot is often called elemental carbon (EC). On the contrary, black carbon (BC) is used in connection with atmospheric light-absorbing carbonaceous aerosol (Bond et al. 2006). Although EC, BC and soot are often used as equivalents, their definitions are slightly different (Bond et al 2006).

Despite the extensive research over the past decades, soot formation remains a process that is not well understood, especially compared to the formation of inorganic particles (Flagan and Seinfield 1998, Wang 2011). Soot formation is a complex phenomenon in which hydrocarbon chemistry occurs within a flame. Soot has been extensively studied in hydrocarbon flames and in diesel engines; however, few studies have focused on soot emissions from the combustion of solid biomass. According to Richter and Howard (2000), the basic steps for soot formation are as follows. First, the molecular precursors of soot are thought to be heavy PAHs. The growth from small molecules to larger PAHs is thought to involve the addition of C_2, C_3 and some other small units (such as acetylene) to PAH radicals and the reactions among growing aromatic species, such as PAH-PAH radical recombination and addition reactions. The contribution of different types of growth reactions is thought to be fuel dependent. The second phase includes the

nucleation or inception of particles from heavy PAH molecules to form nascent soot particles. Third, nascent soot particles grow due to the addition of gas phase species, such as acetylene and PAHs. Next, soot particles agglomerate due to reactive particle-particle collisions. Although the mass remains constant during this process, the particle number decreases in conjunction with an increase in particle size. For longer residence times and under pyrolytic conditions in the postflame zone, polycyclic aromatic compounds undergo functional elimination, cyclization, ring condensation and ring fusion, which is attributed to dehydrogenation and the growth and alignment of polyaromatic layers. This process converts the initially amorphous soot material into an increasingly more graphitic carbon material with a slight decrease in the particle mass. Finally, the oxidation of PAH and soot particles is a process that competes with the formation of the species. Oxidation decreases the mass of PAHs and soot through the formation of CO and CO_2. Oxidation of soot in diffusion flames occurs after the formation process. However, in pre-mixed flames, the formation and oxidation processes occur simultaneously. The main oxidation reactants are OH (most important in fuel-rich flames), O and O_2 (most important in fuel-lean flames) (Richter and Howard, 2000). Because soot formation cannot be avoided in diffusion flames, the oxidation of soot is especially important for controlling soot emissions (Wiinikka and Gebart, 2004, Furuhata et al. 2012). Soot particles oxidize and burn rapidly when they pass through the flame front. However, very fast dilution with cold air may lead to soot emissions despite the presence of oxygen (Flagan and Seinfeld, 1998). Roughly spherical primary soot particles with diameters of 10-50 nm typically form chained agglomerates (Wentzel et al. 2003) (see Figure 3).

Recent studies have suggested that lignin decomposition products play an important role in soot formation from wood combustion (Baeza-Romero et al. 2010). Soot from biomass combustion differs from hydrocarbon soot and contains more oxygenated functionalities, such as o-PAHs, than hydrocarbon soot (Fitzpartick et al. 2007, Baeza-Romero et al. 2010). Many of these compounds can be attributed to the original fuel. Furthermore, the larger observed oxygen contents in biomass emission particles make these particles more hydrophilic and, therefore, more active as cloud condensation nuclei (Picaud et al. 2004), can change the particle optical properties (Mochiad et al. 2004) and can change the potential for causing adverse health effects (Sklorz et al. 2007). Soot has been considered to be a component of particulate matter

that absorbs light. However, recent investigations have reported that organic coatings on particles can increase the light absorption efficiency, indicating that organic compounds contribute to the light absorption capabilities of PM (Schnaiter et al. 2005, Shiraiwa et al. 2010, Heringa et al. 2011).
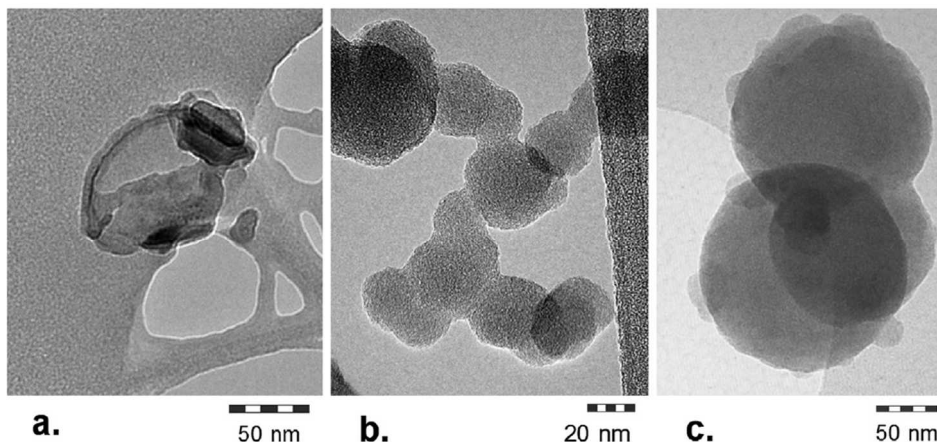
Figure 3. Typical morphologies in a specific combustion system (Transmission emissions microscopy images; Torvela et al. 2014): (a) a typical ash particle, (b) primary particles in a soot agglomerate and (c) particulate organic matter.

3.3.2 Organic emissions

The main components of wood are cellulose, hemi-cellulose and lignin. A complex mixture of volatile organic compounds (VOC) and POM is emitted from wood combustion in both the gaseous and particulate phases (McDonald et al. 2000, Tissari et al. 2007) due to incomplete combustion (Figure 3). The main organic compounds of biomass combustion are monosaccharide derivates from the breakdown of cellulose (Simoneit et al. 1999), which has characteristics that depend on the temperature of the cellulose decomposition (Simoneit 2002). Other important organic components of biomass smoke include alkanes, resin compounds, anhydrous sugars, phenols, lignans, and PAHs (Simoneit et al. 1999, Hays et al. 2011, Orasche et al. 2012, 2013).

Due to their carcinogenicity, PAHs are a well-known group of organic compounds that are contained in combustion emissions (Boström et al. 2002,

Tapanainen et al. 2012, Jalava et al. 2012). Residential wood combustion is one of the largest sources of PAHs (Tissari et al. 2007, Hytönen et al. 2009, Bari et al. 2011). PAHs are formed in the oxygen poor area of the flame, which is where polymerization occurs instead of oxidation; the emissions are greatly affected by the combustion efficiency (Johansson et al. 2004, Tissari et al. 2007).

Dilution in the atmosphere and in sampling systems affects the partitioning of semi-volatile organic compounds between the gas phase and particulate phase. Gas-particle partitioning occurs via absorption with an organic solution or adsorption to soot or inorganic particles. When the dilution ratio increases further, a portion of the semi-volatile organic compounds evaporate, which reduces the particle mass (Lipsky and Robinson 2006).

Once in the atmosphere, volatile organic species can contribute to SOA formation (Robinson et al. 2007). Organic compounds go through reversible phase partitioning, deposition and chemical reactions with oxidant species. Organic aerosol becomes more oxygenated during aging, less volatile and more hygroscopic (Jimenez et al. 2009). SOA is formed when volatile species have sufficiently low volatility to partition to the particle phase. Wood combustion, which is an important source of organic aerosols and VOC, has been identified as a source of SOA both in laboratory experiments and in the atmosphere (Grieshop et al. 2009, Heringa et al. 2011, Elsasser et al. 2012).

Traditionally, all light-absorbing material in the atmosphere has been considered soot (or black carbon). However, there is evidence that some organic matter has light-absorbing effects. Therefore, the term "brown carbon" has been suggested for light-absorbing organic matter (Andreae and Gelencsér 2006). Brown carbon interferes with the measurement of black carbon in many situations, especially regarding biomass combustion aerosol measurements.

3.3.3 Fine fly ash particles

Fine fly ash particles from wood combustion are formed from inorganic ash-forming elements in the fuel that volatilize at typical combustion temperatures and form particles when the flue gas cools or via chemical processes in the flue gas; primarily alkali metal chlorides, sulfates and

carbonates are formed (e.g. Valmari et al. 1998, Tissari et al. 2007, Sippula et al. 2007). Fine fly ash particles are important not only in industrial-scale combustion but also in continuously operated residential-scale appliances, such as small pellet burners and boilers, where OC and EC particle emissions are low. In woody biomass combustion, the most important released elements include alkali metals (primarily K and Na), S, Cl, P and some heavy metals, such as Zn.

In hot flue gas, volatilized species form very small particles via homogenous nucleation; these particles grow via coagulation and additional condensation of vaporized ash-forming elements. At high temperatures, agglomerated particles may coalescence into dense spheres. However, after combustion, the gases cool below the melting point of the condensed material, the liquid freezes and sintering effectively stops. Torvela et al. (2014) suggested that in Zn rich fuels, ZnO particles from Zn vapor would be the first particles to form, most likely in the oxygen-rich secondary combustion zone, and act as a nucleus for other fine fly ash condensation. ZnO formation is followed by gas-to-particle conversion of alkali sulfates, carbonates and chlorides. Collisions among the solid particles produces chain-like agglomerates (such as those in Figure 3), which are common features of aerosol particles that are produced by vapor nucleation in high-temperature systems (Flagan and Seinfeld, 1988, Torvela et al. 2014).

Alkali metals play an important role in the formation of fine fly ash particles. It has been shown that the concentration of alkali metals in fuels can correlate with the concentrations of alkali metal compounds that are found in the particles (Sippula et al. 2007). However, not only the concentration of ash-forming elements in the fuel but also the release of ash-forming elements affect emissions from different fuels. The release is primarily affected by the fuel bed temperature and the fuel ash chemical composition (Dayton et al. 1995, Baxter et al. 1998, Knudsen et al. 2004, van Lith et al. 2006). Previous studies have shown that higher Cl contents in fuels lead to increased fine particle emissions (Lind et al. 2006, Tissari et al. 2008a); however, in S-rich fuels, alkali metals tend to form alkali sulphates instead of alkali chloride. Alkali sulphates are less volatile and are more likely retained in the bottom ash, which leads to fewer problems on heat exchanger surfaces because these compounds are less sticky (e.g. Lind et al. 2006, Sippula et al. 2008). A fraction of K also reacts with silicates that are present in fuels to form potassium silicates, which are not as volatile as potassium chlorides or

sulfates. However, potassium silicates (and other alkali silicates) melt at relatively low temperatures and may cause slagging problems in the fuel bed (Baxter et al. 1998, Khan et al. 2009). The release behavior of ash-forming elements can also be influenced by additives, which have been used to capture alkali metals in the coarse ash fraction. The use of kaolin as an additive has been studied in biomass fuels for inhibiting the formation of corrosive KCl fumes and particles or for decreasing the slag formation by increasing the ash deformation temperature (Steenari et al. 1998, Aho 2001, Davidsson et al. 2007, Khalil et al. 2011). The use of additives in residential appliances has been shown to reduce PM emissions (Tissari et al. 2008a, Sommersacher et al. 2013). For example, the mixing of biomass fuels and peat has been used to reduce gaseous KCl, KCl deposits and fine particle emissions (Kassman et al. 2013, Näzelius et al. 2013, Fagerström et al. 2014).

Laboratory studies of different biomasses conducted in controlled environments have shown that the release of different elements varies greatly with the combustion temperature. At temperatures less than 500 °C, Cl is primarily evaporated (van Lith et al. 2006), although smaller quantities of organically associated K may also be released (van Lith et al. 2008). K and Na are not released in large quantities from fuels for temperatures less than 700 °C (Jensen et al. 2000, van Lith et al. 2008); however, the release of these elements increases sharply between 800 °C and 1150 °C, respectively (van Lith et al. 2008). At temperatures exceeding 800 °C, K interacts with silicates in the ash and affects the release (van Lith et al. 2008). S release has been found to occur in two phases. First, a fraction of S is released at temperatures less than 500 °C, which is due to the decomposition of organic S compounds. At temperatures between 850 °C and 1150 °C, inorganic S is gradually released (van Lith et al. 2006). Some heavy metals, such as Zn and Pb, are also found in biomass fuels (Jones et al. 2014) and vaporize at combustion temperatures exceeding 500 °C (van Lith et al. 2008). The vapor subsequently forms particles. The release increases with increasing combustion temperature (Jimenez et al. 2008, Wiinikka et al. 2013). Some metals behave like alkali metals; their release can be reduced by changing the S/Cl ratio of the fuel (Sippula et al. 2008).

In addition to problems in the atmosphere that are induced by fine particle emissions, inorganic components in biomass fuels are connected with several disadvantages in combustion processes. In residential-scale appliances, fine particles may cause deposition on heat exchangers and slag formation on

grates, which disturbs the combustion process (Baxter et al. 1998, Öhman et al. 2004, Lindström et al. 2007, Gilbe et al. 2008). Formation of slag may impair combustion conditions and cause emissions of carbonaceous species or even operational shutdowns. In addition to the aforementioned problems, in fluidized bed combustion, fine fly ash particles may also cause agglomeration of fluidized bed material, heat exchanger fouling and high-temperature corrosion (e.g. Baxter et al. 1998, Khan et al. 2009).

3.3.4 Particle emission factors

Particle emission levels from residential combustion appliances can vary significantly according to the combustion technology, fuel and combustion control. For example, emissions from burners and boilers fueled with wood logs and pellets have been reported to vary between 13 and 23 mg/MJ; the minimum and maximum values are 4.6 and 44 mg/MJ, respectively (Obaidullah et al. 2012). Extremely low PM_1 emissions have also been reported from a prototype gasification combustion pellet burner (2.4 mg/MJ, Nuutinen et al. 2010). In older boiler types and when agricultural biomasses are used, PM emissions can be as high as 2200 mg/MJ for old wood log boilers (Johansson et al. 2004) and 215 mg/MJ for rape straw pellets (Carroll and Finnan 2013). Moreover, some operational inadequacies can further increase the emissions (Schmidl et al. 2011).

Modern automated appliances are designed to function continuously for different power demands, which has decreased the need for startup and shutdown procedures. However, combustion conditions during low load operation are not optimal with respect to the combustion chamber design, leading to increased PM emissions and incomplete combustion conditions (Johansson et al 2004, Tissari et al. 2008a, Boman et al. 2011, Verma et al. 2011, Schmidl et al. 2011). Schmidl et al. (2011) reported that EC emissions increased in low load operation, whereas less fine fly ash were found in PM compared to full load operating conditions. Some studies have also reported that the increase in emissions due to decreased power may also be very small (Schmidl et al. 2011, Johansson et al. 2004).

In batch combustion, particle emissions are dominated by emissions from incomplete combustion, including soot and organic material (Tissari et al. 2007). The formation of these species is influenced by both combustion

technology and user behavior (Tissari et al. 2009). In modern batch combustion appliances, these emissions always occur, whereas in automatically operated pellet appliances, especially in large-scale combustion units, emissions originating from incomplete combustion are very low.

3.3.5 Gaseous emissions

In addition to particle emissions, many gaseous compounds are also emitted during combustion. These compounds include CO_2, CO, NO_x, SO_x, and the aforementioned gaseous hydrocarbons. CO_2 is a greenhouse gas that is always released in combustion process despite the combustion quality. Carbon monoxide, CO, is an intermediate product of carbon oxidation to CO_2, and CO formation occurs in fuel-rich regions of the flame. The CO emissions are determined by the oxidation of CO (mixing, temperature and O_2 concentration) and not the formation in the flame. In modern residential appliances, e.g., pellet appliances, CO and hydrocarbon emissions are low (Nussbaumer 2003). CO toxicity is particularly important in household appliances. CO can cause fatal poisoning if released in enclosed spaces (Omaye 2002). Eventually, CO oxidizes to CO_2. However, together with VOCs and NO_x, CO contributes to tropospheric ozone formation.

In biomass combustion, NO_x emissions (NO and NO_2) are formed via several pathways. The most important mechanism in biomass combustion is the formation of NO_x from fuel-N, whereas thermal-NO_x formation does not play a significant role due to the relatively low combustion temperatures (Flagan and Seinfeld, 1998). NO and NO_2 are among of the most important molecules in atmospheric chemistry. NO is rapidly oxidized to NO_2 in the atmosphere, causing acidification in the environment. NO_x in atmosphere is involved in several chemical reactions and contributes to, e.g., in the formation of SOA and tropospheric ozone. Moreover, N_2O is formed during the combustion process. N_2O is a very strong greenhouse gas (Solomon et al. 2007) and takes part in ozone depletion (Ravishankara et al. 2009). NO_x emissions in residential biomass combustion are generally low because both combustion temperatures are low and wood fuels are low in nitrogen; however, NO_x emissions may increase when other types of biomass fuels,

such as agricultural biomasses, are used because these fuels have higher N contents (Rabacal et al. 2013).

Sulfur oxides, i.e., SO_2 and SO_3, are formed during the combustion of sulfur-rich fuels; the formation is affected by the S contents of the fuel (Carvalho et al. 2013). Biomass fuels are rich in alkali metals, which bind with S and Cl and prevent the emissions of SO_2 and HCl. Thus, molar ratios of the fuel (K+Na)/(Cl+2S) that exceed one are known to indicate low SO_2 and HCl emissions (Jensen et al. 2001, Sommersacher et al. 2012). SO_x is harmful to both human health and the environment and causes corrosion in materials (Flagan and Seinfeld, 1998). Acidification of forests is the best known effect of SO_x emissions. Moreover, SO_x emissions have been problematic, especially those originating from industrial processes. Sulfur contents in biomass fuels are generally low; therefore, SO_2 emissions are not a major concern (Vassilev et al. 2010).

3.4 Emission reduction in biomass combustion with primary and secondary measures

Several measures have been applied to reduce emissions from combustion processes based on unit sizes. Although similar principles can be used in both residential- and industrial-scale appliances, their usability varies according to the application. The optimization of combustion appliances is often a tradeoff between efficiency and emission control (van Loo and Koppejan 2008). Here, emission control in residential-scale appliances is primarily discussed. The most common primary emission reduction measures include the optimization of air staging, the optimization of combustion chambers, and the modification of fuel (van Loo and Koppejan 2008) by blending different fuel raw materials or by additives (Tissari et al. 2008a).

Air staging can be used for optimizing the combustion process, which reduces emission of both incomplete combustion and NO_x (van Loo and Koppejan, 2008). Air staging has been used in large units for decades to control temperatures in the flame and in the fuel bed. Recently, air staging has also become common in residential combustion appliances, especially in logic-controlled appliances equipped with λ sensors, such as wood chip boilers and pellet boilers. In addition to λ sensors, combustion processes can

be further monitored with thermocouples, CO sensors or draught measurements; the data obtained from these monitoring devices can be used for more precise control (Obernberger and Thek, 2010).

In large units, air staging has been primarily applied to reduce NO_x emissions (Khan et al. 2009, Houshfar et al. 2013). In automated residential appliances, similar techniques for controlling combustion and reducing emissions are being used. In batch combustion appliances, air staging is used to improve the combustion quality (Nuutinen et al. 2014). When combustion air is fed in two stages, the primary combustion air flow can be reduced. This slows the gasification of the fuel and creates both a separate zone for the gasification of the fuel and a secondary combustion zone in which combustion gases are efficiently burned out (Tissari 2008, van Loo and Koppejan 2008).

Optimized air staging can also reduce fine fly ash emissions, although the effect of air staging on particle emissions has not been widely studied in residential appliances. Wiinikka and Gebart (2005) found that reducing the primary air flow resulted in lower fine particle emissions, most likely due to lower oxygen concentrations in the fuel bed, which resulted in lower temperatures and lower vaporization of ash elements. Furthermore, feeding combustion air solely through the grate as primary air led to a two-fold increase in particle concentrations. In another study by Wiinikka and Gebart (2004), high air-to-fuel ratios resulted in reduced particle emissions, and increased combustor temperatures resulted in elevated emissions of ash particles. Secondary combustion is especially important in biomass combustion, where emissions from incomplete combustion are formed in the flame; these products are later oxidized in the secondary combustion process (Wiinikka and Gebart 2004, Wiinikka et al. 2007, Fernandes and Costa 2013).

Reducing NO_x emissions with air staging is possible using two different mechanisms. First, by maintaining under-stoichiometric conditions during the primary combustion process, it is possible to create a reducing environment in the primary combustion zone, where HCN and NH_3 are reduced to N_2 instead of being oxidized to NO or NO_2 (van Loo and Koppejan, 2008, Khan et al 2009). Second, because combustion air is distributed between the primary and secondary combustion zones, less combustion air is fed to the primary zone, which decreases the temperature and reduces the formation of thermal-NO_x. However, staged combustion for reducing NO_x emissions may lead to elevated emissions of unburnt species

(Liu et al. 2013). In addition, flue gas recirculation can be applied to prevent slagging, improve mixing and control the temperature (Obernberger and Brunner, 2012). General values for optimal conditions in the primary combustion process have been identified (van Loo and Koppejan 2008, Obernberger and Brunner 2012) to ensure reduced NO_x and unburnt compound emissions, i.e., a residence time exceeding 0.5 sec, an excess air ratio less than 1.0 and temperatures of 900–1000 °C.

Several secondary emission reduction techniques have been used in industrial units for reducing emissions of particles and gases, such as NO_x, SO_x, HCl and PCDD/F (van Loo and Koppejan, 2008). ESP, condensing heat exchangers, catalytic converters, baghouse filters, scrubbers and cyclones can be used to reduce particle emissions (van Loo and Koppejan 2008, Obernberger and Thek 2010). Various secondary emission reduction technologies are under development for residential-scale use (Gröhn et al. 2009, Hukkanen et al. 2012); moreover, several ESPs are already on the market (Obernberger and Mandl 2011). With the current status of residential-scale ESPs, high particle removal efficiencies can be achieved in good combustion conditions; however, these systems seldom function efficiently in variable and high-emission systems, such as batch combustion, where the need for reducing emissions is the greatest (Obernberger and Brunner, 2012).

4 METHODS

Most of the work discussed herein was performed at the Fine Particle and Aerosol Technology laboratory, which is located at the University of Eastern Finland. Some of the experiments in Paper IV were conducted in the field. Particle sampling and collection must be carefully prearranged to cover the wide variety of emissions from residential combustion, the requirements of the measurement instruments and the interactions between the gas and particle phases, which is particularly challenging during the aerosol sample procedure due to changing temperatures and concentrations.

Gas and particle emissions were investigated in this work; the physical and chemical characterization of particle emissions was the primary focus of the investigations. A schematic representation of the measurement system is shown in Figure 4.

4.1 Combustion appliances

Small-scale appliances were used in Papers I–III and partially in Paper IV (Table 2, Figure 5). These appliances are typically used for heating rooms or houses. The masonry heaters used in Paper II heat the environment by natural convection and radiation, whereas heat produced by pellet boilers, oil burners, and larger units is transformed to a fluid through heat exchangers, which is used to transport heat to specific locations.

The pellet boiler used in Papers I, II, III and IV was an Austrian-made, automated fixed-grate pellet boiler with an integrated burner and boiler (Biotech PZ-RL 25 kW). The boiler operates using a top feed (also "overfeed") principle, in which the pellets are dropped onto the grate from the top (Figure 2). This technique ensures that the fuel feed is accurately controlled and that the danger of back burn from the furnace to the storage tank is nonexistent. However, dropping new fuel on the burning fuel can disturb the flame, resulting in the release of some larger particles (Fiedler 2004). Automated and well-controlled operations result in relatively low emissions of gaseous species and particles, which was described in the previous chapter. In the

pellet boiler used in this work, combustion air is led in through separate primary and secondary air inlets. Primary air is inserted from the bottom of the combustion chamber through the grate, and secondary air is inserted in the upper part of the combustion chamber, approximately 10 cm above the grate and through 12 secondary air inlets. The combustion air flows were continuously measured in the experiment system used in this study. The total λ and primary and secondary air flows were used to calculate both the primary lambda (λ_{Pri}) and the secondary lambda (λ_{Sec}).
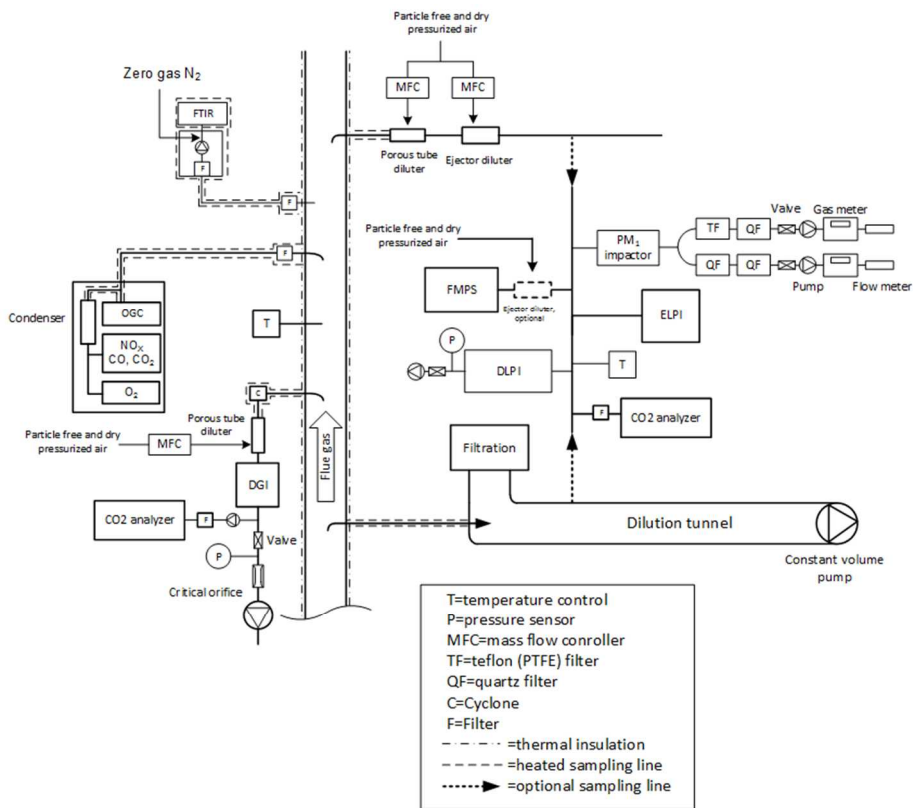

Figure 4. Schematic drawing of the measurement setup.

Conventional masonry heaters are the most common residential combustion appliances for heating individual rooms or houses in Finland. These heaters are typically capable of storing heat for long periods of time with relative steady and low thermal output. Conventional masonry heaters are often made of bricks, soap stone or rock casting material. In these appliances, fuel can be combusted at relatively high burning rates; moreover, heat is stored in the material and released to the surrounding air over a period of several hours (up to 48 h) after the combustion has been stopped (Tissari 2008). Combustion technology in conventional masonry heaters (and in sauna stoves) is rather simple. Wood is inserted on a grate or on the bottom of the combustion chamber; combustion air is primarily introduced through the grate and/or through the door. Flue gases inside the masonry heater first rise and then fall, possibly rising again to ensure a sufficiently long residence time with the heat-storing material (Figure 5). Sauna stoves are operated following a similar principle to conventional masonry heaters. However, sauna stoves are light weight and are designed to rapidly release heat to the surrounding room.

Modern masonry heaters stand out from conventional heaters due to the improvements in the combustion chamber structure and the separation of combustion air into primary and secondary air flows (Figure 5). Secondary combustion air is generally inserted into the upper part of the combustion chamber to improve combustion quality. Additionally, combustion air flow through the grate can be reduced to control the fuel temperature and to prevent excessively rapid devolatilization of the fuel. Reflecting materials can be used in the combustion chamber to increase the temperature and to improve burnout quality. Generally, in modern Finnish masonry heaters, the combustion process exhibits less variability than in conventional heaters. Moreover, both gaseous and particle emissions are lower in modern masonry heaters (Nuutinen et al. 2014). Previous results have indicated that with this technique, the burnout of EC may not be enhanced as efficiently as the other components of incomplete combustion.

A 20 kW light fuel oil burner was used in Paper IV. This burner was equipped with a pressurized atomization system for the fuel, which is commonly used in residential heating systems. The fuel in the light fuel burner was commercial light fuel oil.

Table 2. Explanations of the appliances, fuels and their abbreviations.

|	Abbreviations	Explanations	Appliances	Fuels
Paper I	L_{25}	Nominal output, 25 kW	Pellet boiler, 25 kW	Commercial wood pellet
	$L_{12.5}$	Lower output, 12.5 kW		
	L_7	Lower output, 7 kW		
	$Prim_1$	Primary air 29%		
	$Prim_2$	Primary air 18%		
	Sec_1	Secondary air 83%		
	Sec_2	Secondary air 67%		
Paper II	EFC	Efficient combustion	Pellet boiler, 25 kW	Commercial wood pellet, Birch logs
	IBC/34	Improved batch combustion	Modern masonry heater	
	CBC1	Conventional batch combustion, whole cycle	Conventional masonry heater 1	
	CBC2/F	Conventional batch combustion, firing phase	Conventional masonry heater 2	
	CBC3/23	Conventional batch combustion, 2. and 3. batch	Conventional masonry heater 3	
	IEBC/S	Inefficient batch combustion/starting phase	Sauna stove	
Paper III	W1		Pellet boiler, 25 kW	Wood pellet
	W4			Pine bark pellet
	P2			Peat pellet
	WP2			40% Peat – 60 % Pine bark
	WP3			20 % Peat – 80 % Pine bark
	S1			Rye straw
Paper IV	Wood chip	Wood-chip-fired heating plant	10 MW	Wood chip and sawdust
	LFO	Light fuel oil burner	20 kW	Light fuel oil
	HFO	Heavy fuel oil burner	5.2 MW	Heavy fuel oil
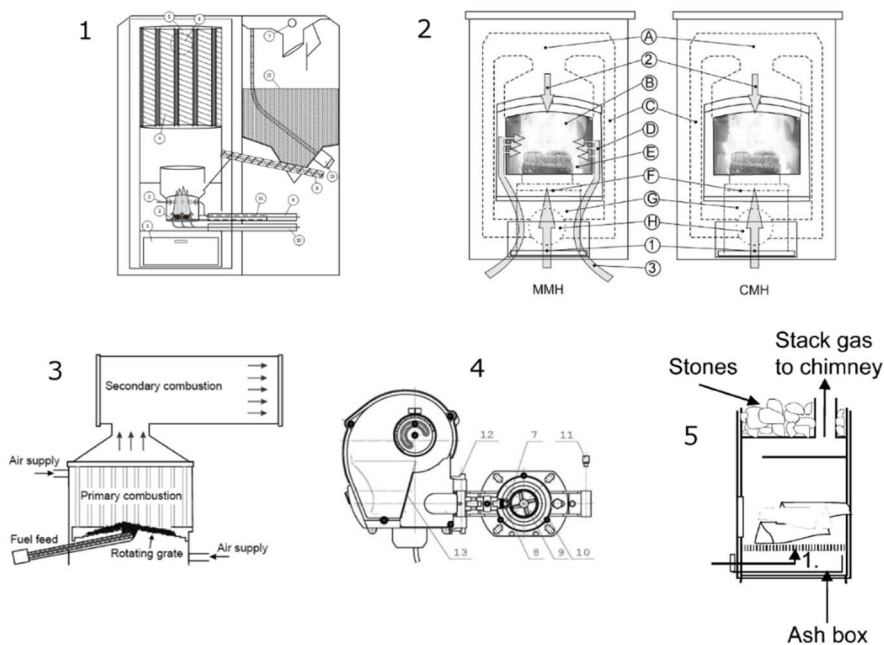
Figure 5. Schematics of the combustion systems (not to scale): a modern pellet boiler (1, Paper I), a modern masonry heater (MMH) and a conventional masonry heater (CMH) (2, Nuutinen et al. 2014), circulating grate combustion technology (3, Sippula et al. 2009b), a light fuel oil burner (4, Oilon Home Ltd) and a sauna stove (5, Tissari et al. 2007).

4.2 Particle measurement and characterization

Sampling is an important part of studying fine particle emissions, especially in small-scale combustion, i.e., where organic compounds can be present in large quantities. Some semivolatile organic species are in present in the gas phase in hot flue gas; however, these species partly condense later on existing particles when the temperature is reduced. Moreover, if samples are obtained from hot flue gas, PM emissions can be substantially underestimated (Nuutinen et al. 2014). In this work, dilution was always used prior to sampling to reduce temperatures, water contents and concentrations and to ensure that the sample better represented the atmospheric conditions.

In Papers I and III (and the secondary dilution system used in Paper II), a partial flow dilution tunnel (built according to ISO 8178–1) was used as a primary dilution system. In this system, a portion of the flue gases are transported from the chimney to the dilution tunnel through a heated sample line (Figure 4). The pressure and flow in the tunnel can be adjusted to control the dilution ratio. The flow was maintained at approximately 650 m^3/h in the tunnel during this work. Laboratory air was used as dilution air in the tunnel; this air was filtered to remove particles, organic compounds and nitrogen oxides.

The primary dilution and particle collection system that was used in Papers II and IV was a porous tube diluter (PRD) (Lyyränen et al. 2004) connected to a Dekati gravimetric impactor (DGI) (Table 3) (Dekati Ltd., Tampere, Finland). The system is described in detail in Ruusunen et al. 2011. The system was designed to be compact and capable of collecting PM for particle characterization and toxicological analyses. The DGI is a five stage cascade impactor (four impaction stages and a back-up filter), which is operated with a 70 lpm flow. The back-up filter and two filter stages were pooled together; these samples were used in the chemical analyses.

The secondary dilution system was a combination of a PRD and an ejector diluter (ED) (Dekati FPS-4000, ejector only) in Paper II, where filter collections were made after the PRD+ED (Table 2). Similar filter collections were made in Papers I and III in the dilution tunnel. Impactors (Dekati PM10 impactor) (Dekati Ltd., Tampere, Finland) were used before the filter collection to remove particles with the size exceeding 1 µm (Figure 5). As described in Sippula et al. 2007 and 2009b, particles were sampled on 47 mm PTFE and quartz plane filters. This collection system was used for the subsequent analysis of organic carbon (OC), elemental carbon (EC) and carbonate carbon (CO_3). Moreover, ICP-MS and IC analyses were performed from the PTFE filters in Papers I and III. OC, EC and CO_3 were analyzed using a thermal-optical method with an analyzer manufactured by Sunset Laboratory Inc. (OR, USA) (Birch and Cary 1996) and based on the National Institute for Occupational Health NIOSH 5040 procedure (NIOSH 1999). OC is typically present in the particle phase as organic matter (OM). The correction factor for changing OC (i.e., the total amount of carbon in OM) to OM varies from 1.2 to 2.5 (Turpin and Lim 2001, Aiken et al. 2008) based on the individual particle properties. For simplicity, OC results are not converted to OM; instead, the results are presented as OC.

Particle mass-size distributions were measured using a 13-stage Dekati low-pressure impactor (DLPI) (Dekati Ltd., Tampere, Finland). The DLPI collects particles with diameters between 30 nm and 10 µm at a 10 lpm flow rate. Aluminum foils were used for impaction plates; the aluminum was greased with a mixture of toluene and Apiezon-L vacuum grease to prevent bouncing. The foils were heated to 105 °C before being weighed to evaporate any extra toluene. Similar foils were used in the pre-cutoff impactors before filter collections.

Particle number-size distributions were measured using two different analyzers, i.e., an electrical low-pressure impactor (ELPI) (Dekati Ltd., Tampere, Finland) and a fast mobility particle sizer (FMPS) (TSI Inc., MN, USA) (based on Tammet et al. 2002). The structure of the ELPI is similar to the DLPI; particles are divided into 13 different size classes using inertial impaction (Keskinen et al. 1992). Additionally, particles are charged in the ELPI with corona charger. When the particles hit the impaction plates, they lose the charge; this charge is measured by the electrometers. The ELPI used herein operates with a 10 lpm flow and measures particles with diameters between 30 nm and 10 µm. When equipped with a filter stage, particles with diameters as small as 7 nm can be observed. Due to its wide measurement range, 1 Hz time resolution and robustness, the ELPI is often used in combustion studies. Particle classification in the FMPS is based on particle electrical mobility. The FMPS is operated with a 10 lpm flow and measures particles with diameters between 5.6 nm and 560 nm (split into 32 size classes). The FMPS also measures with 1 Hz resolution. However, contrary to the ELPI, the FMPS operates at atmospheric pressure. Moreover, the measurements are focused on smaller particles.

Different chemical analyses were performed using the PM_1 samples, including metals, ions and PAHs. ICP-MS was used for analyzing metals, and an IC was used to analyze ions. The PAH analysis included 30 different PAHs. The analyzed PAHs included 16 from the United States Environmental Protection Agency (US EPA 1984) priority pollutant list and 14 from the genotoxic PAHs set by the World Health Organization (WHO-ICPS 1998). A detailed description of the analysis and the analyzed compounds is presented in Paper II. Briefly, PAH compounds were quantified and compared against a mixture of standard compounds. Additionally, deuterated PAH compounds were used as an internal

surrogate standard; these compounds were analyzed using a gas chromatography-mass spectrometer (GC-MS, Agilent).

Fuel compositions were analyzed using various methods. For biomass fuels, moisture contents, ash contents, heating values, ash deformation temperatures, and elemental compositions were analyzed. In the analyses of elements, different digestion methods were used, including nitric acid dissolution (also in a microwave oven (EPA3051)) and fluoric acid–nitric acid dissolution. These samples were analyzed with ICP-MS or ICP-AES. A more detailed description of the fuel analyses is presented in Paper III.

4.3 Measurement of gaseous emissions

Gaseous components were primarily measured using two different instruments. An ABB Hartman & Braun gas analyzer system (ABB Cemas Gas Analyzing Rack, ABB Automation GmbH, Germany) was used to continuously measure O_2, CO, CO_2 and NO_x. This system also included a flame ionization detector (FID) for measuring organic gaseous compounds (OGC). Furthermore, a Gasmet DX-4000 (Gasmet Technologies Ltd., Helsinki, Finland), which is based on a Fourier transform infrared (FTIR) spectrometer, was used. This apparatus is capable of measuring H_2O, CO_2, CO, NO, NO_2, N_2O, SO_2, NH_3, CH_4, HCl, HF, and different VOCs, which are especially common in combustion flue gases. The instrument was equipped with an additional O_2 sensor. CO_2 concentrations were also continuously measured in the diluted samples for calculating the dilution ratio (DR) (Figure 4).

Table 3. Particle sampling and measurement systems.

	Paper I	Paper II	Paper III	Paper IV
	Lamberg et al. 2011	Lamberg et al. 2011	Lamberg et al. 2013	Kaivosoja et al. 2013
Source/appliance	Pellet boiler	Pellet boiler, MMH, CMH, and SS	Pellet boiler	Pellet boiler, oil burner, wood chip fired plant, and HFO
Fuel	Commercial softwood pellet	Pellet and birch logs	Pellets of several different raw materials	Pellet, wood chips, LFO, and HFO
Primary sampling system	Partial flow dilution tunnel	PRD[1] PRD+ED[2]	Partial flow dilution tunnel	PRD
Secondary sampling system		Partial flow dilution tunnel[3]+ED[4] PRD+ED+ED[5]		PRD+ED+(ED)
Primary (and secondary) DR	102–124(–1220)	13–26[1], 14–35[2], 88–128[3], 790–810[4], and 280–385[5]	106–187	7.1–65
PM collection	Filter collection (PTFE+quartz) and DLPI	Filter collection (PTFE+quartz), DGI, and DLPI	Filter collection (PTFE+quartz) and DLPI	DGI
PM chemical analyses	OC/EC, anions, and elements	OC/EC, anions, elements, and PAHs	OC/EC, anions, and elements	Anions, elements, and PAHs
Particle number-size distribution	ELPI and FMPS	ELPI	ELPI	

5 RESULTS AND DISCUSSION

5.1 The effect of operating conditions on emissions in a pellet boiler

Modern pellet boilers are capable of using different loads without having to turn the boiler on and off, which has reduced the need for ignitions and shutdowns in real-life operations and has reduced emissions. In typical pellet combustion systems, combustion air flows and fuel inputs are automatically regulated according to needed output powers. Because the combustion chambers and operation are designed to function optimally on nominal loads, changes in fuel and air flows can be expected to affect the combustion conditions at low loads. In Paper I, decreasing the load resulted in slight increases in PM_1 emissions, i.e., from 12.2 mg/MJ to 13.1 and 15.7 mg/MJ when the load decreased from 25 kW to 12.5 kW and 7 kW, respectively. The increase in CO emissions was more evident, i.e., from 64 mg/MJ to 132 and 178 mg/MJ, respectively. These results agree with previous results (Schmindl et al. 2011, Boman et al. 2011). Even small changes in the emissions for different loads may become important with strict emission limits that also account for partial load conditions in type testing. The PM_1 composition revealed that most of the increase in PM_1 emissions was due to increased EC emissions, whereas inorganic emissions exhibited only a slight decrease. Boman et al. (2011) also reported increased PAH emissions for low loads. Interestingly, Figure 6 shows that the PM_1 chemical profile was very similar for low load (L_7), in reduced secondary air (Sec_2) and from modern batch combustion, although the PM_1 emissions exhibited some variability. Increased emissions for low loads were most likely due to higher air-to-fuel ratios in the pellet boiler, especially in the primary combustion zone. Excess air in the fuel bed and in the combustion chamber can reduce the temperatures in the combustion chamber and weaken the oxidation of combustion gases (Gungor 2010). Furthermore, secondary air may lose its capability of penetrating the primary combustion gases, which further reduces oxidation (Koksal and Hamdullahpur 2004). Overall, the emissions

for low load conditions remained substantially lower than the emissions from batch combustion in Paper II.

In the experiments where different air settings were investigated, decreasing the secondary air (while keeping the total lambda roughly constant) increased incomplete combustion emissions, especially CO in the gaseous phase and EC in the particle phase. With the lowest secondary air inputs, i.e., where the input was decreased by 33% from the normal setting, the PM_1 emission was 29 mg/MJ, which was approximately 2.4-times higher than when operated with the factory settings; an increase in CO emissions was even more substantial. The decrease in the secondary air flow inputs were 17% and 33%, and their effect on both particle and gas phase emissions were substantial, indicating that even rather small changes in combustion settings can lead to significantly increased emissions.

Reducing the amount of primary air through the grate resulted in lower PM_1 and CO emissions. The primary air was reduced from 174 lpm to 50 lpm and 15 lpm. However, even with such large primary air reductions, the PM_1 emissions were 5.4 mg/MJ and 3.1 mg/MJ, respectively. The decrease in PM_1 emissions is related reductions in both EC emissions and alkali metals. The decrease in PM_1 emissions from 12.2 mg/MJ to 3.1 mg/MJ indicates a considerable emission reduction potential for optimized staged combustion. However, in the context of reducing emissions, the amount of primary air cannot be reduced below certain point without sacrificing the efficiency of the boiler. In the present work, output power of the boiler was not continuously measured; instead, the load with reduced primary air settings was estimated using the total air flow to predict that the output power decreased from 25 kW to 19 kW and 17 kW. However, by redesigning the grate and combustion chamber, it is possible to maintain low primary λ while simultaneously producing the desired amount of heat. In the boiler used herein, the secondary air inlets were relatively close to the grate; therefore, it is possible that secondary air could have created a back flow and was consequentially involved in primary combustion. There were no tools available to study this behavior in more detail. However, the very low primary λ indicates that there may have been additional combustion air in the primary combustion zone, which could have resulted either from leaks or back flow from the secondary air input.

Particle emissions originating from incomplete combustion, especially EC in Paper I, and K and SO_4 originating from the fuel exhibited large

contributions to the total PM_1 emissions. When the combustion conditions deteriorated, EC became the most prominent component contributing to the PM_1 emissions; only a slight and insignificant increase in OC emissions occurred. The increased PM_1 emissions through increased EC emissions were similar for partial loads and when secondary air was reduced (Figure 6 and 7). However, for nominal load conditions, the EC emissions were already low; further reductions in EC emissions did not play an important role in reducing the total emissions. Therefore, reducing PM_1 emissions using reduced primary air inputs was largely related to the decreased K and SO_4 emissions. Temperatures on the grate or on the fuel bed were not measured; however, the reduced air flow through the fuel bed may have resulted in reducing conditions and lower fuel bed temperatures, which suppressed the release of alkali metals. Previous results by Wiinikka and Gebart (2005) support these findings. However, in other types of appliances, a considerable increase in primary air caused lower volatilization of inorganic species due to the lower temperatures in the fuel bed (Obernberger and Brunner 2012). Air staging was also used for controlling NO_x emissions; however, in the present system, no effect was observed because the combustion chamber geometry was likely not ideal for reducing NO_x. The primary and secondary combustion zones were not properly separated to ensure both sufficient residence time and the presence of a reduction zone between the combustion zones, which would enable the reduction of NO_x to N_2.

Both the amounts and distributions of primary and secondary air were varied in the experiments, including the partial load tests and the air reduction tests. Various parameters and correlations were determined based on these experiments. These results revealed that the ratio of primary and secondary combustion lambdas (λ_{Pri} / λ_{Sec}) was more important than combustion air flow alone. Figure 8 highlights the correlations between λ_{Pri} / λ_{Sec} and emissions of CO, PM_1, K and EC.
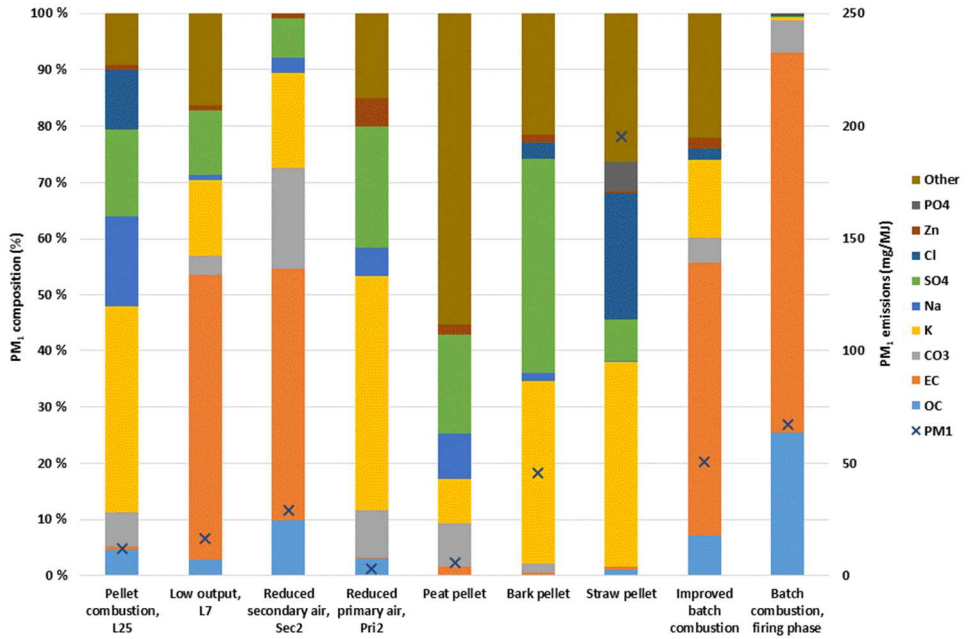
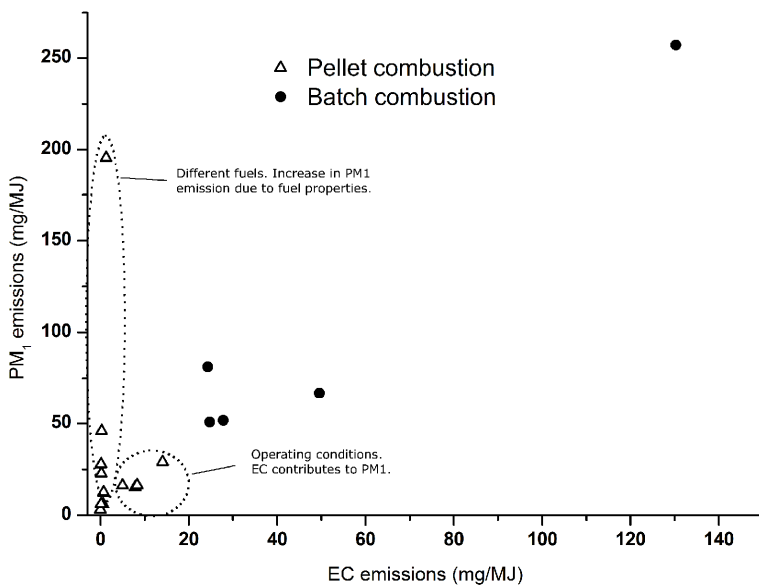*Figure 6. PM₁ emissions and compositions in selected experiments.*

Figure 7. Correlations between EC and PM₁ emissions in different experiments.
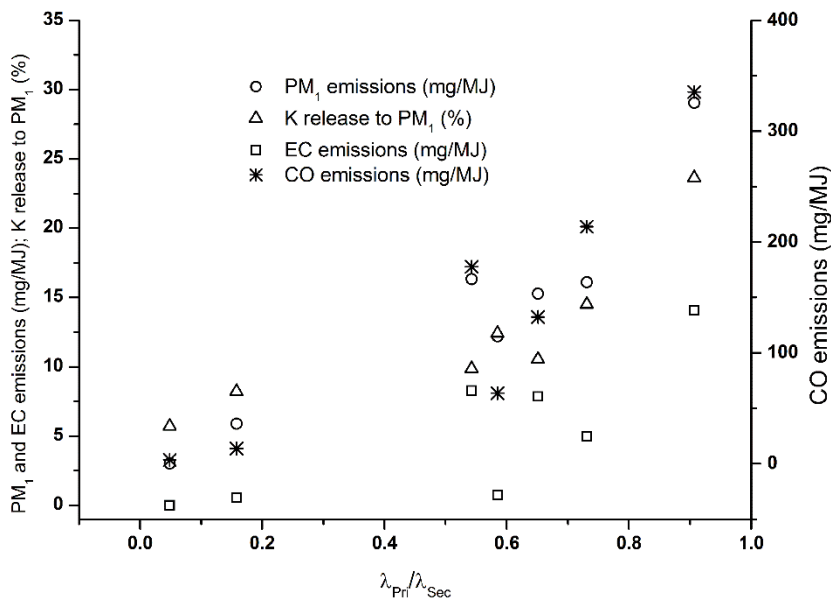
Figure 8. Correlations between $\lambda_{Pri}/\lambda_{Sec}$ and the emissions of PM_1, EC and CO (mg/MJ) and the release of K to PM_1 (%).

5.2 Emissions from a residential pellet boiler compared to batch combustion appliances

Particle emissions from batch combustion appliances contain considerable amounts of EC and OC that originate from incomplete combustion. Furthermore, particle emissions and particle characteristics were found to vary significantly between different combustion appliances and combustion conditions. PM_1 emissions from the studied pellet boiler (Paper II) were 19.7 mg/MJ and primarily composed of inorganic species. The highest PM_1 emissions were measured from the starting phase of a sauna stove (257 mg/MJ). Combined with the firing phase in conventional batch combustion (CBC2 in Table 2), the PM_1 emissions from these two conditions were almost

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entirely composed of EC and OC, whereas the emissions of particle phase inorganics were low (Figure 6). CO emissions were 5 to 50 times higher in the studied batch combustion appliances than in the pellet boiler, although the air-staging technology in the modern masonry heater resulted in lower CO emissions than in the batch conventional combustion devices used in Paper II. However, the effect of improved combustion technology was not as evident in the PM_1 emissions as in the CO emissions. The most significant difference in emissions between the different combustion appliances and combustion conditions were found in the particulate PAH emissions (Figure 9; Paper II: Table 7). The starting phase of a sauna stove produced the highest PAH emissions, whereas the studied pellet boiler produced the lowest PAH emissions. The PAH emissions behaved in a similar manner to the emissions of a few other compounds, such as OGC; however, PAH emissions were found to be the most sensitive compound to combustion conditions. As a result, the combustion technology affected the PAH emissions more than PM_1 and CO emissions. Toxicological studies (Jalava et al. 2010, Oh et al. 2011, Tapanainen et al. 2012) have shown that the amount of PAH in PM can correlate with the toxicology of the PM_1; therefore, there may be a direct relationship between combustion conditions and health effects.

A direct comparison between the different batch combustion appliances is not straight forward based on the results presented in this thesis due to the differences in the appliances and combustion situations. However, secondary air, or staged combustion, is an important component of controlling emissions in both automated and batch combustion appliances. Old-fashioned appliances are equipped with only one combustion air input or air is led into the system in an uncontrolled manner (typically through the grate and/or the door). Applying automation and fan-assisted combustion air inputs may further improve the combustion quality and reduce the harmful emissions generated in incomplete combustion. Batch combustion is naturally highly variable compared with continuous combustion, such as pellet boilers, making the optimization of the process more complex. In Finnish masonry heaters, such as those used in this work, combustion air input is unforced. This condition most likely leads to situations where combustion air flows are not sufficient for all conditions. Moreover, by maintaining flows that are suitable in some conditions leads to too much air flow for other combustion conditions. More precise combustion air controls would lead to reduced emissions.
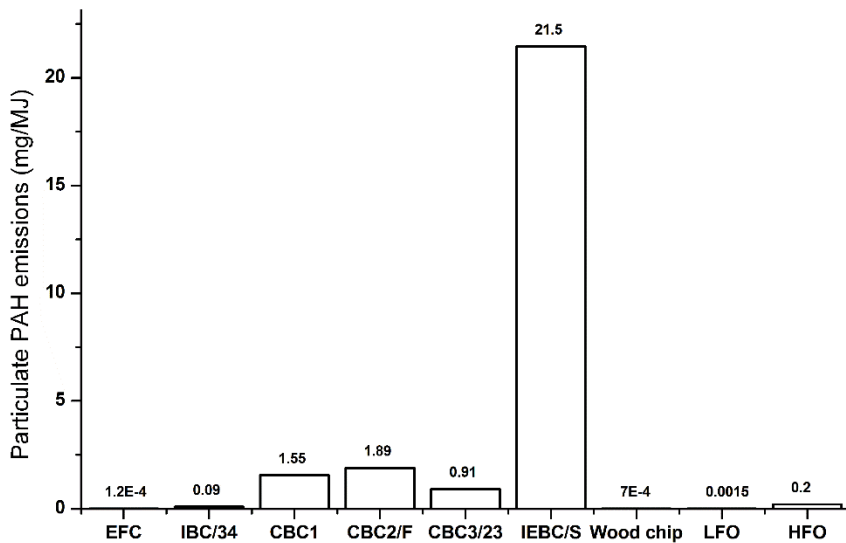
Figure 9. Particulate PAH emissions from different combustion sources.

5.3 Emissions from different pellet raw materials

PM_1 emissions from different pellet materials varied substantially, ranging from 5.1 mg/MJ (for peat pellet) to 195 mg/MJ (for rye straw pellet) (Figure 6). Generally, peat pellets produced the lowest PM_1 emissions and were found to decrease PM_1 emissions when mixed with woody biomass. PM_1 emissions from different pellet raw materials were primarily composed of K, SO_4 and Cl. Significant amounts of PO_4 were observed in the PM_1 emissions from straw pellets (Figure 6). The highest PM_1 emissions were measured for straw pellets; the fuel characteristics of straw pellets are substantially different than the other studied pellet fuels. Some fuel properties, such as the contents of K+Na+Cl and K correlated with PM_1 emissions, and the (K+Na)*2Cl/S molar ratio in the fuels correlated with the sum of K and Na in PM_1. These indicate that these elements in the studied fuels directly affected

the formation of PM_1. For example, bark contains relatively high amounts of K and Na; therefore, the use of bark in fuels (for example in forest residues or tree including bark) increases particle emissions.

Two independent factors, i.e., the fuel Si content and the fuel Cl/S ratio, affected the release of ash-forming elements and PM_1 emissions. Si forms alkali metal silicates with alkali metals, which are less volatile than alkali metals chlorides and sulfates; these compounds are more readily maintained in the bottom ash, suppressing their release (Knudsen et al. 2004). Previous studies have also reported that Cl increases the release of alkali metals (Knudsen et al. 2004, Lind et al. 2006), but there are other studies that have supported the finding that S may decrease the release of alkali metals, especially in Cl-rich fuels (Lind et al. 2006, Sippula et al. 2008). Because peat contains more Si and S than woody biomass, the use of peat as fuel to decrease PM_1 emissions can be due to either of these two processes, or a combination the two. However, based on the results, it was not possible to define which process (or if a combination of the two processes) caused the decreased PM_1 emissions. Although Si prevents the release of alkali metals by forming alkali metal silicates, these alkali silicates decrease the ash melting temperature and can create problems in the usability of the fuel by producing ash melt on the grate.

Pellet raw materials did not have a significant effect on gaseous emissions originating from incomplete combustion. However, some operational problems, primarily due to ash melt formation on the grate, disturbed combustion air flows and increased the CO and OGC emissions. Both the CO and OGC emissions were lower when peat-wood mixtures were used than with woody biomass pellets; therefore, the addition of peat to woody biomass improved the combustion conditions. Peat and straw produced the highest NO_x emissions; the addition of peat to woody raw materials increased the NO_x emissions. The highest SO_2 emissions were also measured in peat pellet combustion. Gaseous emissions originating from fuel quality, i.e., NO_x and SO_2, were directly affected by the pellet fuel properties. Straw pellets were the only fuels to create notable HCl emissions. The fuel $(K+Na)/(Cl+2S)$ molar ratio was found to be a good indicator of SO_2 and HCl emissions (Jensen et al. 2001, Sommersacher et al. 2012).

The use of peat fuel is not straight forward in residential combustion for various reasons. Peat was found to decrease the PM_1 and CO emissions when mixed in pellets with woody biomasses; however, peat also increased the

gaseous NO_x and SO_2 emissions. Additionally, peat increased the fuel ash content, which can create problems, especially in residential appliances that are designed for low-ash content fuels. Furthermore, peat is not a renewable fuel. The use of peat may be an acceptable additive if small quantities of peat resulted in notable decreases in emissions, which may provide more possibilities for using alternative pellet raw materials in residential-scale appliances. Moreover, previous studies have shown that peat has contributed to rising CO_2 concentrations in the atmosphere and perishing natural ecosystems. The studied wood-peat mixtures contained relatively large (up to 40%) fractions of peat; no systematic analysis was performed for different quantities of peat mixed with woody biomass. Tests with mixtures of peat and woody biomass using reduced amounts of peat are needed to better evaluate the use of peat as an additive for reducing emissions. Yet, peat additives could improve the usability of high alkali content biomass fuels in residential-scale appliances.

The PM_1 emission factors from straw pellets were as high as the emissions from incomplete batch combustion (Figures 6 and 7). Additionally, the PM_1 emissions factors from bark pellets were similar to improved batch combustion, although the particle composition was different. The PM_1 emissions from peat combustion were similar to the PM_1 emissions in optimized pellet boiler emissions when commercial pellet fuel was used (Paper I). Consequently, the use of such fuels in residential pellet combustion may lead to PM_1 emissions that are similar to those from batch combustion. Moreover, despite the lower emissions originating from incomplete combustion, the use of modern combustion technology may not lead to lower emissions. Thus, the utilization of the studied alternative pellet raw materials requires flue gas after-treatment systems. Moreover, based on the current combustion technologies that are available on the market, it is advisable to use these types of fuels in industrial-scale units, i.e., which apply flue gas after-treatment procedures; therefore, excessive particle emissions can be avoided.

5.4 Comparison of renewable and fossil fuels in small and medium scale

The PM_1 emissions (0.1 mg/MJ) from a 20 kW light fuel oil (LFO) boiler were substantially lower than those from the studied pellet boiler; these emissions consisted of EC and SO_4 (Paper IV), which is typical for this appliance type (Hays et al. 2008). Moreover, the CO emissions were low (below the detection limit of our analyzer), and the NO_x emissions were nearly the same as those produced by the studied pellet boiler. Previous work has suggested that replacing fossil fuels in residential combustion with biomass fuels can lead to increased particle and gaseous emissions (Johansson et al. 2004); the results presented herein support this finding.

The emissions from industrial-scale heat production unit fueled with wood chips were found to be low due to efficient secondary emission reduction measures, which resulted in emissions that were slightly higher than from LFO but substantially lower than from the studied pellet boiler.

Energy power plants with a size approximately 10 MW are part of decentralized heat production and produce heat for district heating; these power plants are occasionally connected to a specific industrial process. In this work, the PM emissions from wood-chip-fired power plant before the ESP were high; however, after the ESP, particles were effectively removed. However, in operational situations in which the ESP is not functioning properly, PM emissions can be momentarily up to several hundreds of mg/MJ. Similar to the pellet boiler emissions, the PM_1 emissions were primarily composed K and SO_4; the emissions from incomplete combustion were low. Although the PM_1 emissions were lower, the PAH emissions were slightly higher than from the pellet boiler. This result is surprising because the process in industrial-scale operations is very well controlled and equipped with flue gas after-treatment measures.

Heavy-fuel-oil-fired (HFO) burners are typically used in industrial processes and in district heating for producing heat during peak hours and days. Due to very different fuel characteristics, previous studies have shown that HFO emissions were found to be substantially different than wood chip and LFO combustion emissions; however, these emissions exhibit a few similarities, e.g., the large SO_4 fraction (England et al. 2007, Sippula et al. 2009a). The PM_1 emissions from the studied HFO burner were 20 mg/MJ,

which was similar to that of the pellet boiler. SO_4 was identified as the most abundant compound in the particles. A large fraction of the PM_1 was unidentified; however, this fraction likely consisted EC, OC (England et al. 2007, Sippula et al. 2009a) and particle-bound water (Moldanová et al. 2009). Furthermore, some heavy metals were identified; vanadium was the most prevalent. Furthermore, the PAH emissions were even higher than from improved batch combustion (Figure 9). Additionally, the NO_x emissions were higher than from the combustion of stem wood (logs or pellets; Figure 13), whereas the SO_2 emissions derived from the high sulfur contents in the fuels were higher than from any other studied case.

An overall comparison and evaluation of the emissions originating from different heat production systems is very cumbersome. On one hand, bioenergy should be favored to reduce the use of fossil fuels and the production of CO_2 emissions. On the other hand, both gaseous and particle emissions from biomass combustion in residential appliances are larger than from LFO combustion (Paper IV, Johansson et al. 2004). Some emissions, such as SO_2 and NO_x, can be significantly higher in fossil fuel combustion, especially when heavy fuel oils are used. It was also shown in Paper IV that the PAH emissions from wood pellet and wood chip combustion were lower than from the combustion of light and heavy fuel oils. Present legislation for PM emissions are based on particle mass; even though the composition has been linked to the harmfulness of PM, the PM composition is not included in these regulations (Becker et al. 2005, Sklorz et al. 2007, Jalava et al. 2007, Tapanainen et al. 2012).

5.5 Additional examination of the particle emissions

5.5.1 Composition of PM_1 emissions in different combustion experiments

EC and OC constituted a significant fraction of the PM_1 emissions from batch combustion appliances and from the studied pellet boiler when combustion conditions were not optimal (Figure 6). OC was primarily present in the PM_1

emissions from batch combustion appliances, especially when the combustion conditions were extremely poor. Although the amount of OC from batch combustion decreased when the combustion conditions were improved, it was more challenging to reduce the EC emissions (Figures 6 and 7). This behavior was evident in both batch combustion appliances and in pellet combustion. In Paper II, two similar combustion appliances were studied; one appliance represented conventional technology, and the other appliance represented modern technology. The use of modern technology substantially affected the CO, OGC and PAH emissions, but the EC emissions were the same from both appliance types. This behavior in batch combustion was recently reported by Nuutinen et al. 2014. Nevertheless, emissions originating from incomplete combustion can be affected by further optimizing combustion technology. Similar to batch combustion, EC emissions were substantial from the studied pellet boiler with low loads and with reduced secondary air; the PM_1 emissions were increased almost entirely due to increased EC emissions (Figures 6 and 7). Both decreased temperatures and less efficient mixtures of secondary air and combustible gases most likely led to the reduced oxidation of EC and the increased emissions. Similar behavior was also reported by Schmindl et al. (2011) using a pellet boiler under non-optimal conditions. The awareness and importance of EC emissions has recently increased, especially in Nordic countries because EC — in addition to direct climate warming effect — can accelerate the melting of Arctic ice if deposited on the surface of the ice (Bond et al. 2013, Meinander et al. 2013, Jiao et al. 2014).

Paper III presented very different PM_1 emissions from various pellet raw materials. However, the PM composition was found to be very similar in the different fuels despite the different PM_1 emissions (Figure 10). The share of K in the PM_1 emissions was approximately 30% in more than half of the experiments and between 10% and 20% for the other fuels. The proportion of SO_4 varied slightly more, i.e., from 15%–40%, with an average of approximately 20% (excluding the straw pellets). Furthermore, the share of CI was rather constant, varying from a few percent to 15% (exceeding 20% for straw). If OC, EC and CO_3 were excluded (not shown), K and Na accounted for approximately 30–35% of the PM_1 emissions (varying from 20% to 45%). Similarly, SO_4, CI and NO_3 accounted for 20%–50% of the PM_1 emissions. PO_4 was important only in PM_1 samples originating from straw pellet combustion (Paper III, Table 6). Based on all of the experiments

presented in this work, K represents approximately 20–40% of the total inorganic PM emissions (excluding the two poorest batch combustion cases in Paper II) when the carbonaceous components (OC, EC and CO_3) were excluded from the analysis.
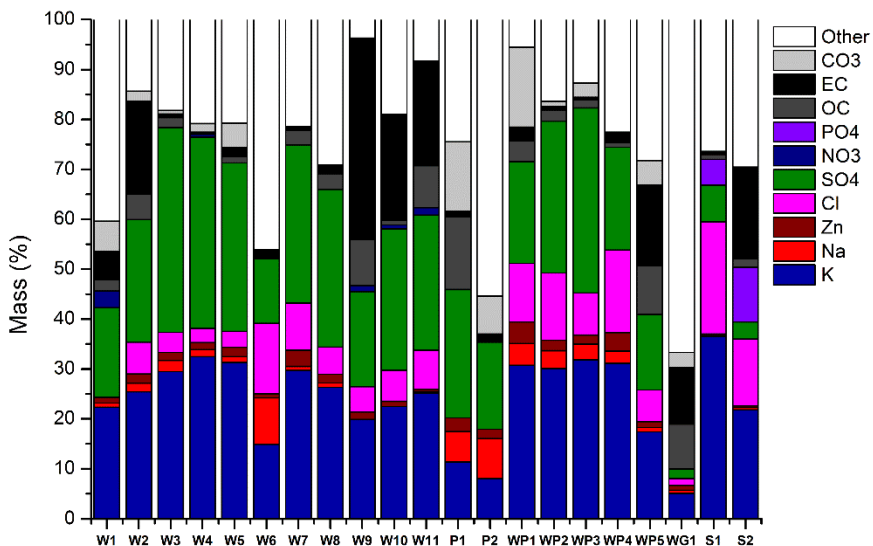

Figure 10. PM₁ compositions for the experiments with different pellet fuels.

5.5.2 Particle number emissions and particle size

Particle number emissions from residential biomass combustion are generally high with smaller particles compared to industrial-scale biomass boilers. The aerodynamic diameters were typically less than 1 μm (Figure 11). Notable amounts of particles with diameters exceeding 1 μm may occur only in very poor combustion conditions and in large appliances.

Batch-wise combustion is naturally highly variable and particle number emissions and particle sizes vary over time. Variation in measured emissions is also present in batch-wise combustion processes from one experiment to another. Thus, identification of uncertainties in limited number of experiments is challenging. Moreover, pellet combustion generated stable

number of particles throughout the combustion process compared with batch combustion processes; however, the reduction of secondary air and lower load conditions also made the pellet combustion process less stable (Appendix I: Figure 1). Ash particles are of special importance in biomass combustion; their number emissions are high. Some ash species formed seed particles, but the other condensing species condensed on existing particles rather than forming new particles through nucleation. Previous work has suggested that ZnO may act as a nucleus in fine fly ash particles (Torvela et al. 2014). The particle number emissions were not correlated with combustion conditions or PM emissions, which has been reported also in previous studies (Johansson et al. 2004, Tissari et al. 2008b). Moreover, the particle number emissions were not correlated with the fuel ash content when different biomass fuels were used (Paper III). Although the number emissions were not related to the combustion conditions, the particle sizes (GMDs) increased with increasing PM_1 emissions.
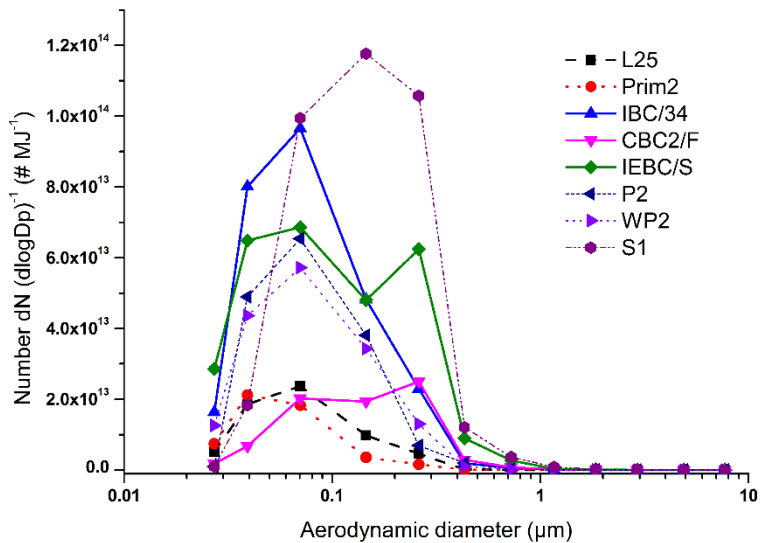

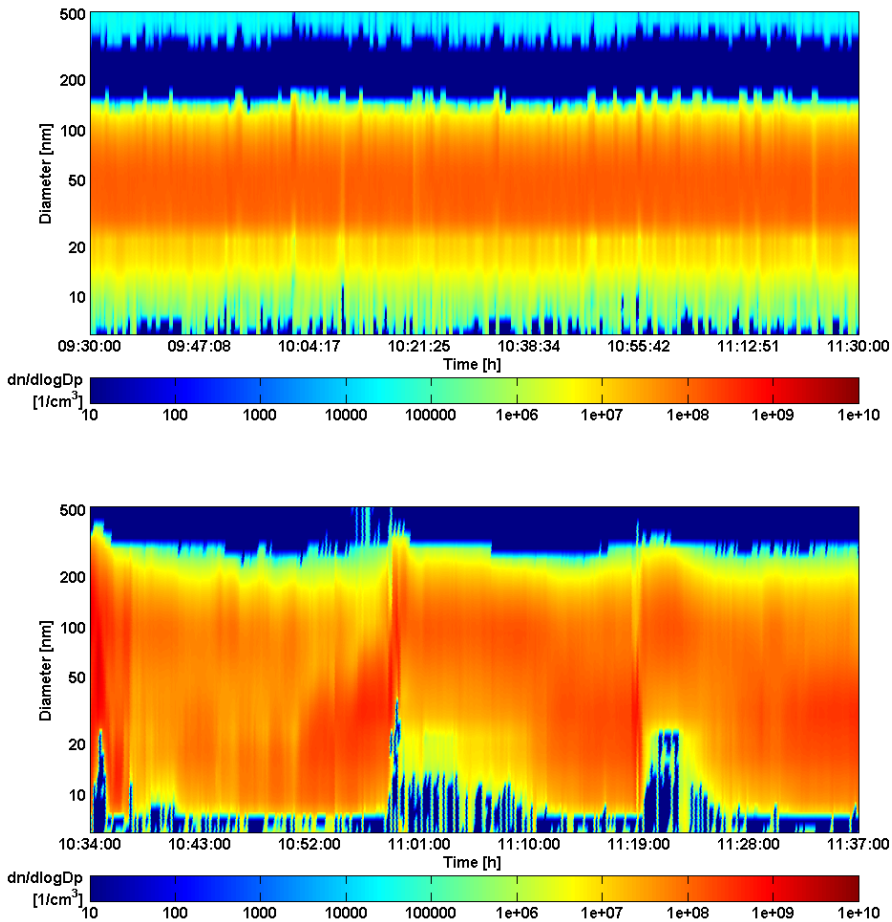*Figure 11. Number-size distribution for different experiments as measured with the ELPI.*

Figure 12. Particle number-size distributions for the pellet boiler with nominal output (L$_{25}$, top) and for the conventional masonry heater (CBC3, bottom).

5.7 Emissions with respect to emission regulations

Currently, there are no PM emission limits for residential combustion in Finland; however, there is ongoing work devoted to creating a Europe-wide (Ecodesign Framework Directive 2009/125/EC, Lot 15: Solid fuel small combustion installations; Lot 20: Local space heating products) emission limit

for residential wood combustion. These regulations will also affect the policies in Finland. Currently, units larger than 1 MW have emission limits in Finland that contain PM regulations (Valtioneuvoston asetus 2013). However, emission limits for residential wood combustion are already applied in many parts of Europe.

Most of the standard measurements are performed with a so-called hot filter sampling, where particles are collected in a hot flue gas onto a hot filter. This technique prevents the collection of most organic phase compounds, which condense first when the flue gas cools to the ambient air temperature and subsequently contribute to primary PM emissions in real-life situations (Lipsky and Robinson 2006). Thus, particles collected from diluted and cooled sample gas are typically desired because they better reflect the conditions in ambient air. Dilution is also required for online particle measurement devices. The dilution tunnel method is used in standard measurements in Norway; however, different operational practices make a comparison with this work even more challenging (Norwegian standard 1994). Despite the differences in measurement methods and their possible effects on emissions, the emission limits form a baseline for emission comparisons. In addition, total suspended particles are measured using standard techniques, whereas PM_1 (also PM_{10} with the DLPI) was sampled in this work. PM_1 was selected because these particles are generated through gas phase processes in the combustion process and cover the main mode of PM emitted from residential combustion.

Pellet appliances typically incorporate modern combustion technology with low emissions. The NO_x emissions from residential appliances are fuel derived, and the combustion technology does not have a major effect on the emissions (Rabacal et al. 2013). There are technological options available to decrease NO_x emissions; however, these options are not yet common in residential-scale appliances. In this work, the NO_x emissions from batch combustion were barely below the limits proposed in the new Ecodesign draft (2009/125/EC, draft Jan 2014 for local space heaters). Moreover, the emissions are also below the emission limit when commercial wood pellets and other pellets that are primarily composed of stem wood were used (Figure 13). When the pellets contained more bark (containing N), such as in logging residues, the proposed Ecodesign NO_x limits were exceeded. The use of peat similarly increased the NO_x emissions above the limit.

The CO emission limits in the Ecodesign proposal have been separated for different appliance types. In the studied pellet boiler, CO emissions were below the emissions limit for most of the tested fuels. Moreover, for mixtures of wood and peat, the emissions were well below the regulations (Figure 13). However, when the combustion conditions were not optimal, the CO emissions may increase, even in automated combustion appliances. This finding was observed with low loads, where the CO emissions slightly exceeded the proposed limit even with the lowest tested load (Figure 13). In the draft of the upcoming standard for biomass boiler testing (Directive 2009/125/EC, Lot 15), partial load tests are also considered, which will most likely lead to increased awareness and to improved appliance designed for handling partial loads.

In Paper II, improved batch combustion with air staging and well-operating conventional batch combustion without air staging emitted less CO than the Ecodesign emission limits, both during the specific combustion conditions and the combustion cycles (Paper II, Table 4). However, the CO emissions from the studied sauna stove with simple combustion technology substantially exceeded the emission limits for CO.

A comparison of PM emissions to the proposed emission limits is more complicated than comparing gaseous emissions due to the previously described sampling issues. Based on current knowledge, it is believed that the effect of different sampling methods on the PM results is smallest for pellet appliances due to a lack of or scarcity of organic compounds. Additionally, stable combustion does not exhibit the problem related to the use of different sampling periods. The studied pellet boiler was considered to be state-of-the-art in 2007 and remains on the market today. The PM_1 emissions for nominal output conditions and with reduced primary air input were below the Ecodesign emission limit; however, at low loads, the PM_1 emissions exceeded the limits (Figure 14). As described previously, the use of different pellet raw materials increased PM_1 emissions, whereas the emissions from pellets composed primarily of stem wood remained below the Ecodesign emission limit. Therefore, such emission limits make the use of alternative raw materials highly improbable if flue gas after-treatment techniques are not successfully applied in residential-scale appliances. Because the use of bark also increased NO_x emissions, ESP alone may not be sufficient to reduce emissions according to the regulations; moreover, NO_x reduction techniques should be applied. In addition, ENPlus regulates the

use of different raw materials, requiring only stem wood and chemically untreated residues from forest industry to be used in the best pellet class, i.e., ENPlus–A1 (EPC 2013).

In current emission measurement standards, different periods of combustion are sampled from batch combustion appliances; the sampling times in this work were not the same as described in any valid standard. All of the PM emissions from tested batch combustion situations using diluted samples exceeded the Ecodesign emission limits. Moreover, the OC fraction from masonry heaters did not exceed 23%, which is not sufficient to explain the difference based solely on the sampling method. It seems likely that many manufacturers will face problems with the new emission limits, especially for particle emissions. Although the number of tested appliances represents only a few types of appliances, it can be concluded that air staging is a good technique to reduce gaseous emission; however, the particle emissions may not be very significantly from the current technology. Because the lifetime of combustion appliances can be as high as several decades, the new emission limits will not have a quick effect on the total emissions. Therefore, other measures should be introduced in conjunction with the new emission limits to hasten the regeneration of combustion appliances.

The legislation only provides limits for specific PM components in a few special cases, such as in waste incineration, i.e., where fuel can be very heterogenic. Directive 2010/75/EC sets limits for certain heavy metal air pollutions from waste incineration; the limit for the sum of $Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V$ is 0.5 mg/m^3 (11% of O_2, which is equivalent to 0.27 mg/MJ). Such elements are not common in clean woody biomass fuels. Nonetheless, the highest values for pellet combustion were approximately 0.35 mg/m^3 in peat pellet combustion. Moreover, from HFO, the emissions of these metals exceeded the limit (0.45 mg/MJ). Furthermore, inhaled zinc is known to be a harmful metal to human health (Fernandez et al. 2001); however, it is not included in the Directive 2010/75/EC. The highest Zn emissions were from straw pellets, whereas the Zn emissions were higher for pellets containing bark than for commercial pellets.
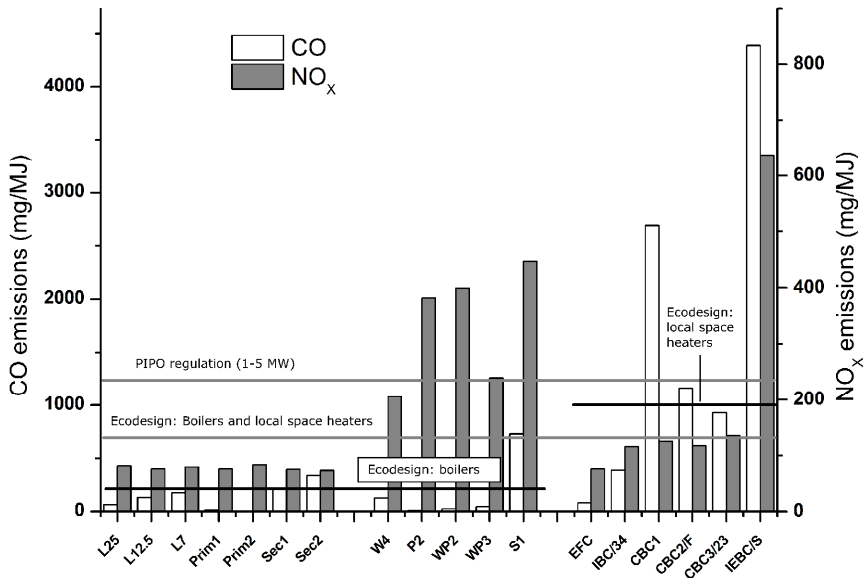
Figure 13. Comparison of gaseous emissions with the different emissions limits. The NOₓ emission limit in the Ecodesign draft is common for local space heaters and solid fuel boilers.
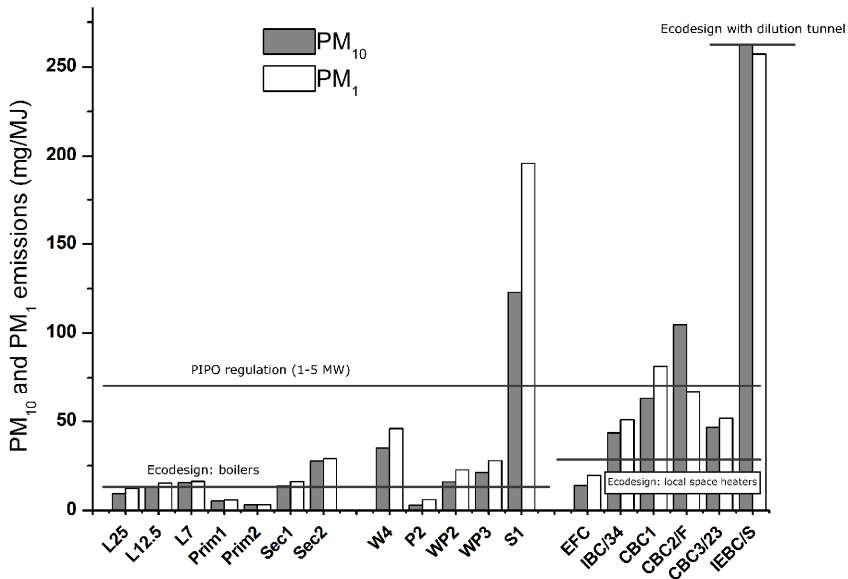

Figure 14. Examples of particle emissions compared with the respective emissions limits. All emission limits are measured in hot flue gas (except with the dilution tunnel), whereas the values presented here are measured in the diluted flue gas.

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6 AUTHOR'S CONTRIBUTION

The research presented in this study was primarily performed at the Fine Particle and Aerosol Technology Laboratory at the University of Eastern Finland between 2007 and 2011.

Paper I analyzed pellet boiler emissions for different operational settings. The experiments were performed in a laboratory environment. The experiments were primarily designed by O. Sippula and J. Tissari. The author was primarily responsible for conducting the experiments and writing the manuscript. The data were analyzed and interpreted by the author with the assistance of O. Sippula and J. Tissari and under the supervision of J. Jokiniemi.

Different combustion conditions were tested for several combustion appliances in Paper II; this study was performed under the supervision of J. Jokiniemi and M.-R. Hirvonen. The experimental setup was designed and constructed by the author with the assistance of K. Nuutinen, J. Ruusunen, J. Tissari and O. Sippula. P. Yli-Pirilä and K. Nuutinen were responsible for the PAH analysis, and the metal and ion analyses were conducted by U. Makkonen, K. Teinilä, K. Saarnio and R. Hillamo at the Finnish Meteorological Institute. The data were analyzed by the author and J. Ruusunen, and the author interpreted the results with the assistance of J. Tissari, K. Nuutinen, O. Sippula, J. Ruusunen, P. Jalava, M. Tapanainen, M.-R. Hirvonen and J. Jokiniemi. The author contributed the most to writing the manuscript.

Emissions from pellet fuels made from different raw materials were tested in Paper III using the same experimental setup as in Paper I. This study was performed under the supervision of J. Jokiniemi. The experiments were arranged by O. Sippula and J. Tissari. The author was responsible for the emission measurements, and the data analysis was performed by the author with the assistance of O. Sippula. The results were interpreted by the author with the assistance of the co-authors. The author was the primary writer of the manuscript.

The experiments for Paper IV were conducted at several locations, which included both laboratory and field sites, under the supervision of J. Jokiniemi

and M.-R. Hirvonen. The author participated in designing and arranging the experiments and performed the pellet boiler, oil burner and wood-chip-fired power plant experiments with the assistance of T. Kaivosoja and A. Virén. T. Kaivosoja and A. Virén were responsible for the heavy fuel oil emission measurements and the PAH analysis of the samples. T. Torvela and U. Tapper were responsible for the scanning electron microscopy. T. Kaivosoja was primarily responsible for writing the manuscript and analyzing the data. The data were interpreted by all co-authors. The toxicology portion of the study was conducted by P. Jalava, M. Tapanainen and M.-R. Hirvonen.

7 CONCLUSIONS

Residential wood combustion is a significant source of fine particle and gaseous emissions around the globe. The emissions vary depending on the fuel, combustion technology and combustion conditions. User operation often affects combustion behavior in residential-scale appliances. In this thesis, fine particle emissions originating from residential pellet combustion were characterized in different operational situations and using different raw materials as pellet fuel. Moreover, pellet combustion emissions were compared with the emissions from other combustion units used for heat production. These experiments included different combustion situations in batch combustion to represent various combustion appliances, combustion phases and combustion technologies, the combustion of light fuel oil in residential-scale appliances, and the use of wood chips and heavy fuel oil in medium-scale energy production.

Generally, the emissions from automated pellet combustion were low (12.2 mg/MJ with wood pellets); the formed particles primarily contained ash, which originated from the volatile inorganic compounds contained in the fuel; alkali metal compounds were the most important. Pellets can be manufactured from different types of woody raw materials and other biomass. Some of these fuels contain high amounts of alkali metals, which were found to produce high fine particle emissions. The emissions from incomplete combustion were low in pellet combustion; however, these emissions increased for some operation conditions, such as a boiler operating at low loads. The PM_1 emissions from a modern pellet boiler running with bark pellets had the same PM_1 emissions as masonry heaters. Thus, the advantage of using a modern pellet appliance may be partially lost if the wrong fuel type is used.

According to this study, several measures can be used to reduce the PM_1 emissions produced in pellet combustion. First, more precise control of the combustion process, such as advanced staging of combustion air, can be utilized to decrease the release of ash particles from the fuel bed. Reducing primary λ while increasing secondary λ was found to result in lower PM_1 emissions (down to 3.1 mg/MJ). Second, peat as an additive may be used in

pellet raw materials to reduce PM_1 emissions. The composition of peat was found to be favorable for inhibiting the release of alkali metals and consequently the formation of fine ash particles. Furthermore, excess PM_1 emissions in residential pellet combustion can be prevented by avoiding the use of fuels that are rich in alkali metals or Cl, e.g., bark or straw.

Both in continuous combustion and in batch combustion, proper combustion technology effectively reduced the emissions of incomplete combustion, such as OC, CO and PAHs. In contrast, it was more difficult to reduce EC emissions. Moreover, when the combustion conditions deteriorated, EC was the first PM component to increase. This phenomenon was highlighted in two separate cases. First, the increased PM_1 emissions for the studied pellet boiler under low load operation was solely due to the elevated EC emissions. Second, there were no clear differences in the EC emissions between conventional and modern masonry heaters even though there was significant effect on the CO, OGC, and PAH emissions. Furthermore, the PAH emissions were more sensitive than other emission components to combustion conditions. Thus, improved combustion technology can affect the harmfulness of the PM via reducing PAH compounds even though the total PM emissions do not decrease.

Optimally operated light fuel oil combustion in a residential-scale burner was not found to be a major source of fine particles (0.1 mg/MJ) due to the efficient combustion process and low amounts of inorganic impurities in the fuel. The PAH emissions from LFO combustion were slightly higher than those of pellet combustion, whereas the PAH emissions from HFO combustion were similar to a modern batch combustion appliance. The emissions from a wood-chip-fired industrial unit were small due to efficient combustion technology and flue gas after-treatment techniques. Such units would also be suitable for alternative biomass fuels because the optimized combustion processes, including flue gas after-treatment techniques, are most likely suitable for high-ash fuels.

This thesis highlights that there are different applications for utilizing biomass fuels for heat production in residential combustion. Current technical solutions provide possibilities for reducing emissions and for using biomass without excess emissions. The emissions from large units are typically well controlled because they are regulated by law. To take full advantage of modern combustion technology in residential-scale appliances, more stringent PM emission limits must be applied. Additionally, because

PM emission limits are set based on their ability to cause adverse health effects, the chemical composition of PM should also be considered. For example, PAH compounds are already monitored in outdoor air; these compounds were shown to reflect the combustion conditions better than particulate mass emissions. A source-based analysis of PAH compounds may provide additional information regarding the potential harmfulness of these emissions.

Continuous combustion appliances, such as pellet boilers and burners, are typically well controlled; however, possibilities remain for reducing the PM emissions under different operating conditions using improved staged combustion. Gasification combustion is an extreme example of staged combustion that has been shown to be beneficial in a small-scale prototype burner. Secondary emission reduction measures, such as electrostatic precipitators, are potentially useful for reducing emissions from residential-scale appliances. These techniques remain under development for residential-scale appliances; their use has not yet been fully demonstrated. ESP technology (or some other secondary reduction technology) should provide emission reductions. First, emissions from existing appliances could be reduced without changing the entire combustion system. Second, high-ash fuels could be used in systems equipped with ESPs without the concern for excess PM emissions. Consumers would be given a choice of either investing in better appliances equipped with an ESP, which comes with the possibility of using low-cost fuels, or purchase a less expensive, yet modern combustion appliance and use first-class fuels. These alternatives would improve the raw material base that is available for pellet production while preventing excess emissions.

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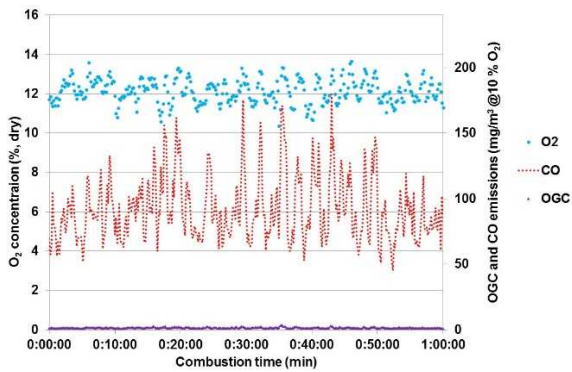# APPENDIX I: TIME SERIES OF GASEOUS COMPONENTS FROM RESIDENTIAL COMBUSTION

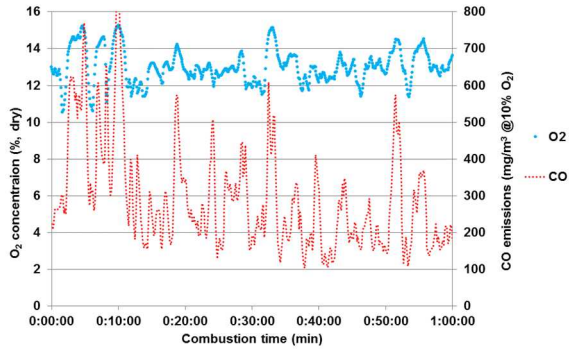*Figure 1: O₂, CO and OGC concentrations as a function of time in the different experimental cases.*
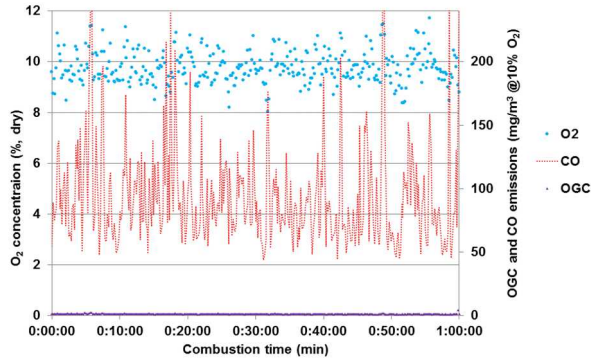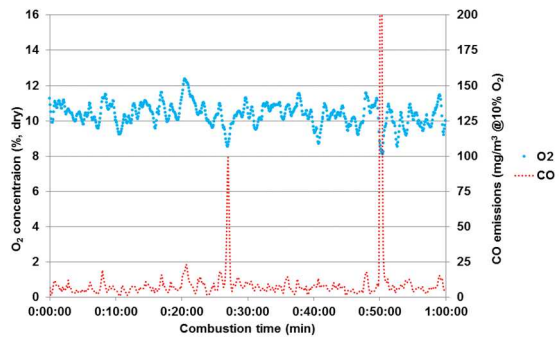

Pellet combustion: peat (20%) and pine bark (80%).
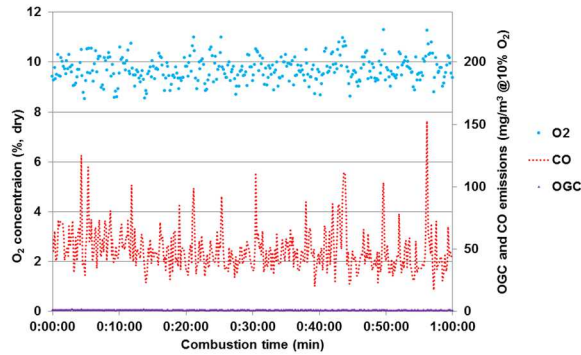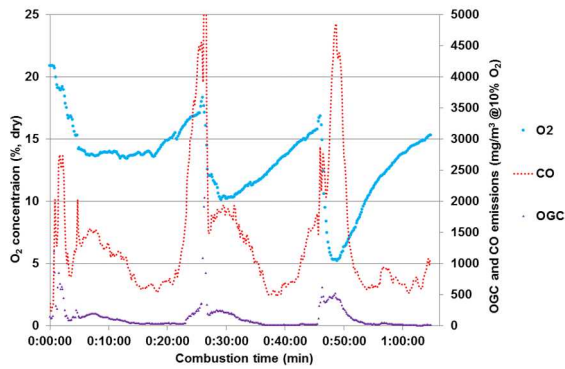

Pellet combustion: peat (40%) and pine bark (60%).

Pellet combustion: nominal load (L₂₅).

Pellet combustion: low load (L$_{12.5}$).

Pellet combustion: reduced primary air (Prim$_2$).

Conventional masonry heater (CBC3).