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FINE PARTICLE AND GAS EMISSIONS FROM SMALL-SCALE BIOMASS COMBUSTION: TEMPORAL VARIATION AND INFLUENCE OF FUEL TYPE

MIIKA KORTELAINEN

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

Academic dissertation

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Author’s Address: Fine Particle and Aerosol Technology Laboratory
University of Eastern Finland
Department of Environmental and Biological Sciences
P.O. Box 1627
FI-70211 Kuopio, Finland
e-mail: miika.kortelainen@uef.fi

Supervisors: Professor Jorma Jokiniemi, Ph.D.
Department of Environmental and Biological Sciences
University of Eastern Finland

Docent Jarkko Tissari, Ph.D.
Department of Environmental and Biological Sciences
University of Eastern Finland

Associate Professor Olli Sippula, Ph.D.
Department of Environmental and Biological Sciences and Department of Chemistry
University of Eastern Finland

Reviewers: Docent Hilkka Timonen, Ph.D.
Finnish Meteorological Institute

Niko Karvosenoja, D.Sc. (Tech.)
Finnish Environmental Institute

Opponent: Docent Aki Virkkula, Ph.D.
Finnish Meteorological Institute

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Kuopio, March 2019

Miika Kortelainen

Fine particle and gas emissions from small-scale biomass combustion: Temporal variation and influence of fuel type

Miika Harri Petteri Kortelainen

University of Eastern Finland, 2019

Abstract

The share of renewable resources in energy production in the European Union (EU) will increase as a result of the EU's climate policy aiming to reduce greenhouse gas emissions. This will probably increase the combustion of solid biomass on both large and small scales. However, increasing biomass combustion is likely to increase the emission of particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs), particularly for small-scale devices—such as stoves, fireplaces and boilers. Since the availability of solid biomass cannot be universally assured, increasing the use of alternative fuels in place of solid biofuels might become a necessity for small-scale combustion. However, these alternative fuels may introduce other kinds of problems, such as further increased particulate emissions and operational problems. Co-combustion of alternative biofuels with wood could mitigate these problems. Furthermore, the utilisation of ashes should be taken into consideration upon implementation of new fuel qualities.

A characteristic feature of small-scale combustion is batch-wise combustion of wood in heaters, which is a popular way of heating detached houses, particularly in Nordic countries. This form of heat production may become more common as new climate policy takes effect. The batch combustion process is highly dynamic and emissions vary accordingly. However, the effect of fuel on the temporal variation of emissions from batch combustion has not been studied thoroughly.

Aims of this thesis were to determine the effect of biomass fuel on emission factors and emission properties and to investigate the temporal variation of particle and gas emissions originating from small-scale combustion appliances. Blending of wood with agricultural fuels was investigated in a 40-kW continuous combustion reactor equipped with a reciprocating-grate burner. The effect of wood species on batch combustion emissions and their temporal variation was studied using a modern heat-retaining masonry heater.

The chemical composition of the fuel was found to be the governing factor in emission formation. In particular, the high contents of potassium and chlorine in agricultural fuels had an increasing effect on PM emissions. Additionally, both reed canary grass and straw have high silicon content, which affects the ash fusion temperature and alkali metal release. The co-combustion experiments indicated that co-combustion of reed canary grass and wood chips is conceivable in small-scale devices, which are capable of operating with fuels containing a moderate amount of ash. However, the co-combustion of straw and wood chips caused notably high particulate emissions and operational problems. Overall, straw combustion in small-scale combustion devices cannot be recommended without efficient flue gas after treatment. The amount of harmful metals in bottom ash did not increase due to combustion of agricultural fuels compared to wood chip combustion and it was fulfilling the Finnish national requirements for forest and field fertilizers.

The differences in batch combustion emission factors between wood species were considerable. The average PM_1 emission of birch was more than three times that of spruce. In batch-wise combustion, efficient mixing of secondary combustion air and devolatilisation products was found to decrease PM_1 emissions. Time-resolved analysis showed that differences mostly reflect the release of refractory black carbon (rBC) and organic emissions, which were the main PM components. Fast ignition from the top of the batch decreased the first batch total organic emissions compared to slower ignition. This was due to the faster increase in the combustion chamber temperature, which is a highly important factor regulating organic emissions. For the same reason, most of the carbonyl emissions were also formed during the first two batches. The formation of particulate PAHs was also partially different between wood species. PAHs were not only formed during the new batch insertion, when temperature was relatively low, but also during the intense burning phase, along with rBC. The results show that, depending on the combustion appliance, the wood species can make a difference especially on the fine particulate emissions of small-scale batch combustion.

Keywords: aerosols, agricultural fuels, ash, birch, beech, co-combustion, fine particles, grate combustion, masonry heater, reed canary grass, small-scale combustion, solid biofuels, spruce, straw, wood chips

Contents

1 Introduction 9

2 Aims of this study 11

3 Literature review 12

3.1 Current knowledge on small-scale biomass combustion emissions 12

3.2 Solid biofuels 13

3.2.1 Wood fuels 13

3.2.2 Alternative fuels 14

3.3 Influence of fuel raw materials on the applicability of small-scale combustion appliances and combustion emissions 16

3.3.1 Physicochemical properties of solid biofuels 16

3.3.2 Effects of ash-forming elements and trace metals 17

3.3.3 Influence on ash utilisation 18

4 Methods 19

4.1 Fuels 19

4.1.1 Wood logs 19

4.1.2 Wood chips 21

4.1.3 Pellets 21

4.1.4 Agricultural fuels 21

4.2 Combustion appliances 21

4.2.1 Reciprocating-grate boiler 21

4.2.2 Pellet boiler 22

4.2.3 Logwood-fired masonry heater 23

4.3 Sampling 25

4.3.1 Particle sample dilution 25

4.3.2 Filter sampling and analyses 26

4.3.3 Gas-phase carbonyls 26

4.4 Chemical characterisation of emissions 27

4.4.1 Offline analysis 27

4.4.2 Online analysis 27

4.5 Physical characterisation of particulate emissions 28

5 Results and discussion 30
  5.1 Influence of fuel type on combustion emissions 30
  5.2 Emission factors 33
    5.2.1 Gaseous emissions 33
    5.2.2 Particle emissions 35
    5.2.3 Comparison to earlier studies 37
  5.3 Time-resolved emissions during batch combustion of wood 38
    5.3.1 Gaseous emissions 38
    5.3.2 Particle emissions 38
  5.4 Release of ash-forming elements and ash mass balances 42
6 Review of papers and the author’s contribution 45
7 Conclusions 46
References 49

Appendices

I Ash fusion temperatures of fuels

List of publications

This thesis consists of an introductory review, followed by four research articles. In the introductory part, the papers are cited according to their roman numerals. The publications are reproduced with the kind permission of the respective journals.

I **Kortelainen, M.**, Jokiniemi, J., Nuutinen, I., Torvela, T., Lamberg, H., Karhunen, T., Tissari, J. and Sippula, O.: Ash behaviour and emission formation in a small-scale reciprocating-grate combustion reactor operated with wood chips, reed canary grass and barley straw, *Fuel*, Vol 143, Pages 80-88, 2015.

II **Kortelainen, M.**, Jokiniemi, J., Tiitta, P., Tissari, J., Lamberg, H., Leskinen, J., Grigonyte-Lopez Rodriguez, J., Koponen, H., Antikainen, S., Nuutinen, I., Zimmermann, R. and Sippula, O.: Time-resolved chemical composition of small-scale batch combustion from various wood species, *Fuel*, Vol 233, Pages 224-236, 2018.

III Czech, H., Sippula, O., **Kortelainen, M.**, Tissari, J., Radischat, C., Passig, J., Streibel, T., Jokiniemi, J. and Zimmermann, R.: On-line analysis of organic emissions from residential wood combustion with single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS), *Fuel*, Vol 177, Pages 334-342, 2016.

IV Reda, A., Czech, H., Scnelle-Kreis, J., Sippula, O., Orasche, J., Weggler, B., Abbaszade, G., Arteaga-Salas, J.M., **Kortelainen, M.**, Tissari, J., Jokiniemi, J., Streibel, T. and Zimmermann, R.: Analysis of Gas-Phase Carbonyl Compounds in Emissions from Modern Wood Combustion Appliances: Influence of Wood Type and Combustion Appliance, Energy & Fuels, Vol 29, Pages 3897-3907, 2015.

1 Introduction

The current climate policy of the European Union (EU) aims to achieve a considerable increase in the share of renewable energy of the final consumption. The 2030 climate and energy framework (EUCO 169/14) sets a binding EU-level target to increase the use of renewables by 27 % from the 1990 level by 2030. Together with recent fluctuation and uncertainties in crude oil prices, this energy policy has led to an increased utilisation of biomass in heat and power production both in large- and small-scale applications. Biomass includes vegetative materials that were directly derived from photosynthesis and, for example, animal by-products derived indirectly from photosynthesis. Biofuels are considered a renewable energy source (van Loo and Koppejan, 2008). The advantages of biomass compared to fossil fuels are not only environmental but also political; biofuels are estimated to provide more employment than coal and oil (van Loo and Koppejan, 2008). Furthermore, biofuels can reduce the dependency on imported fuels of countries with no fossil fuel reserves. Environmental benefits include the reduction of greenhouse gas (GHG) emissions, as biomass absorbs carbon dioxide from the atmosphere while growing. Although, achieving even nearly neutral carbon balance would require sustainable way of cultivation and low combustion emissions (Tilman *et al.*, 2009). However, biomass combustion in small energy production units can be important source of certain emissions that are known to be harmful for human health, such as particulate matter (PM), black carbon, polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides (NO_X). These emissions are largely dependent on the fuel composition, combustion conditions and the degree of flue gas after-treatment (so-called secondary emission reduction) (Kaivosoja *et al.*, 2013). According to current understanding, the fine particle fraction ($PM_{2.5}$) has especially detrimental effects on human health (Schwartz and Neas, 2000) because of its ability to reach the alveolar region and even the bloodstream; in comparison, larger particles (2.5–10 µm) deposit in larger concentrations in the upper airways (Hinds, 1999). Exposure to fine particulate matter has been shown to induce respiratory and cardiovascular effects (Pope III and Dockery, 2006; Schwartz and Neas, 2000).

Emissions from the main anthropogenic sources of particles (i.e. traffic, industry and stationary combustion sources like heat and power production units) are well regulated. However, for small-scale combustion devices (e.g. fireplaces) regulations are currently lacking in Finland. The EcoDesign Directive (2009/125/EC) sets emissions limits for solid fuel local space heaters and solid fuel boilers in the near future (year 2022 and 2020, respectively) (EC 2015/1189) and thus accelerates the development of appliances. However, the directive does not include existing combustion devices or, for example, sauna stoves. Therefore, reducing particulate emissions from small-scale biomass combustion cannot rely only on the EcoDesign Directive, but requires stricter national emissions limits or improvements to operational practices, i.e. educating end-users about the importance of fuel pre-drying, log size, batch size, and ignition. In addition to primary methods (emission formation is inhibited by e.g. improved process control), secondary methods (already formed emission is removed from flue gas) provide another option for reducing emissions. Secondary methods include filters, cyclones, catalytic converters and electrostatic precipitators (Obernberger and Mandl, 2011), but these solutions often have high investment costs or they are laborious to maintain. Considering the low emission altitude and the fact that emission sources are often located in the middle of residential areas, reducing emissions from small-scale combustion could improve local air quality and thus decrease the number of incidents requiring medical attention or even hospitalisation (Ahtoniemi *et al.*, 2010).

Small-scale combustion of wood is the most popular source of heat for detached houses in Finland and batch-wise appliances are the most widespread combustion devices. In 2016 47 TJ of energy was produced by small-scale wood combustion for heating of detached houses, whereas 37 TJ was produced by electric heating (Statistics Finland, 2018). Batch-wise combustion is a highly dynamic process, in which the mass and chemical composition of the emissions are strongly time dependent. Identifying the problematic combustion phases regarding the emission formation would be advantageous not only for evaluating adverse health and climate effects, but also for the development of low-emission batch combustion appliances and operating procedures.

In addition to increased fine particle emissions, small-scale batch combustion produces higher organic emissions compared to devices with higher efficiency (i.e. continuous combustion like pellet boilers) (Lamberg *et al.*, 2011b). Volatile organic compounds (VOCs) and carbonyl compounds (CCs) are formed during incomplete oxidation of hydrocarbons and are known to induce adverse health effects (Sarigiannis *et al.*, 2011). Furthermore, volatile organic compounds emitted to the atmosphere act as precursors for secondary organic aerosols (SOA), which make a major contribution to the total particulate organic emissions from small-scale combustion (Hallquist *et al.*, 2009). Carbonyls have both direct and indirect toxic effects, as they are a significant source of free radicals, acting as precursors for photochemical oxidants (e.g. ground level ozone) that have toxic effects on both vegetation and people (Atkinson, 2000). However, the emission factors for carbonyl compounds from wood combustion still require knowledge from modern appliances.

The full potential of biomass as an energy source has not yet been realised. However, increasing energy consumption creates a demand for alternative fuels. For small-scale combustion, fuel groups like herbaceous fuels or agricultural fuels are almost completely untapped. Increasing the utilisation of these alternative biofuels in small-scale combustion is not, however, straightforward as it sets different requirements for combustion devices and fuel processing compared to wood combustion, e.g. due to the high content of ash, alkali metals and chlorine. One option for increasing the feasibility of these alternative fuels could be mixing them with good-quality fuels. Co-combustion can improve the combustion quality and thus reduce emissions due to the diluting effect of the good-quality fuel or the associated changes in ash composition (Fagerström *et al.*, 2014; Lamberg *et al.*, 2013; van Eijk *et al.*, 2012). However, it is not currently known how suitable alternative fuels are for small-scale combustion, or how fuel chemistry affects emission formation. Also, the potential issue of bottom ash recycling needs to be considered before extensive use of these fuels can be implemented.

2 Aims of this study

The general aims of this study were: (a) to determine the effect of biomass fuel on emission factors and emission properties, and (b) to investigate the temporal variation of particle and gas emissions originating from small-scale combustion appliances.

For each publication, the more specific objectives were:

- **Paper I:**
    - to compare emission levels and physicochemical properties of particles from continuous combustion of wood and co-combustion of wood and two agricultural fuels;
    - to gain knowledge about the applicability of biomass-biomass mixtures in small-scale combustion;
    - to evaluate the distribution of ash-forming elements between bottom ash and fly ash in fine particulate matter as well as the sensitivity of the experimental results to combustion conditions.
- **Paper II:**
    - to characterise highly time-resolved particulate and gaseous emissions from the small-scale batch combustion of wood, including the influence of wood species.
- **Papers III and IV:**
    - to determine the emission factors from small-scale wood combustion for a variety of emitted organic compounds.

3 Literature review

3.1 Current knowledge on small-scale biomass combustion emissions

Small-scale biomass combustion is known to be problematic due to high particle emissions compared to, for example, light fuel oil combustion (Kaivosoja *et al.*, 2013). In particular, batch-wise combustion of wood is known to generate high PM emissions (Frey *et al.*, 2009; Lamberg *et al.*, 2011a). Secondary emission reduction methods, such as cyclones, filters, catalysts or scrubbers, can be efficient in small-scale systems (Grigonyte *et al.*, 2014; Gröhn *et al.*, 2009; Hukkanen *et al.*, 2012), but are often not applicable or considered too expensive or laborious to maintain for small-scale combustion appliances (Carnö *et al.*, 1996; Hukkanen *et al.*, 2012). A common issue in batch combustion systems is the lack of heat storage, meaning heat output is usually controlled by restricting the combustion air intake (Tissari *et al.*, 2008a). This generally leads to high emissions of incomplete combustion (Johansson *et al.*, 2004; Jordan and Seen, 2005; Tissari *et al.*, 2009; Tissari *et al.*, 2008a). A preferred option is devices with either an external heat reservoir or a heat-retaining structure, which enables a high burn rate but stable heat release. This leads to lower emissions of incomplete combustion as there is no need to restrict the combustion process (Nuutinen *et al.*, 2014). Considering emissions, one challenge in batch combustion is the highly dynamic nature of the combustion process; conditions in the combustion chamber are constantly changing according to the phase of combustion, and certain emissions are known to be strongly dependent on the predominant conditions in the combustion chamber (for example organic emissions). Thus, emissions can vary substantially within a single batch (Elsasser *et al.*, 2013; Eriksson *et al.*, 2014; Heringa *et al.*, 2012). This makes the development of efficient emission reduction techniques for small-scale biomass combustion challenging.

Compared to batch combustion appliances, continuously operated biomass combustion systems represent a more advanced form of small-scale biomass combustion. These appliances are usually used for central heating systems and include boilers and burners designed for either woodchips, pellets or even energy crops (Tissari *et al.*, 2008b). A typical burner technology is the stoker burner, which consists of separate fuel silo, feed screw and a horizontally- or under-fed burner placed inside the firebox. Depending on the fuel and burner, emissions can be relatively low compared to batch combustion devices (Lamberg *et al.*, 2011a). The major advantage of modern, logic-controlled continuous combustion devices is that the combustion process can be constantly adjusted towards optimal combustion. This makes combustion more stable and can reduce the fraction of emissions from incomplete combustion to negligible levels (Lamberg *et al.*, 2011b).

Currently, information on the effect of fuel type on time-resolved emissions from small-scale, batch-wise combustion is quite sparse. More detailed investigation could assist in developing of new, low-emission combustion appliances. Furthermore, due to potentially increasing small-scale biomass combustion, there is a need to assess the environmental impacts of utilising alternative biomass to wood.

3.2 Solid biofuels

3.2.1 Wood fuels

The typical size for wood logs used in batch combustion devices is between 25 cm and 50 cm in length. Larger logs (referred to as billets, ~1 m in length) are mostly used in boilers or large masonry ovens. The recommended moisture content of wood logs is between 15 wt% and 20 wt%. Typically, in Finland, wood logs come from private forests. However, the trade of commercial wood logs has increased, and for commercially available graded firewood, ISO 17225-5:2014 dictates fuel quality classes and specifications. This standard sets mandatory quality requirements for three quality classes (A1, A2 and B). The quality class B is intended mainly for boilers. Standardised qualities include origin and source, wood species, diameter, length and moisture content, and volume or weight. The standard also includes voluntary information, such as energy content, the drying method used, amount of decay or mould, and the split volume proportion (Alakangas *et al.*, 2016). Stove and boiler manufacturers often give a recommendation for fuel quality class for use in their appliances.

In Finland, wood chips are frequently used in heat production on farms or in similar environments where wood is available from private forests and can be chipped on-site. Wood chips are made by chipping larger wood pieces (i.e. whole trees, stem wood, and forest residues) into smaller pieces. Wood chips usually contain bark and possibly entrained inorganic material from harvesting (derived from soil). Typical ash content varies between 0.7 wt% and 2.5 wt% (dry basis, d.b.), while moisture content varies between 30 wt% and 50 wt% (Alakangas *et al.*, 2016; van Loo and Koppejan, 2008). ISO 17225-4:2014 dictates the fuel quality classes and other specifications of graded wood chips. Quality criteria are given for four classes (A1, A2, B1, and B2), with class A1 being recommended for domestic boilers. Specific requirements are given for origin and source, particle size, moisture content, ash content and bulk density of the wood. Voluntary information includes net calorific value and energy density.

Wood pellets are manufactured by compressing the dry, milled by-products of the forestry industry (usually sawdust and shavings) into cylindrical pellets. Usually, no additives are needed to hold the pellets intact as lignin acts as a binding agent. Properties of wood pellets are standardised with an international standard (ISO 17225-2:2014). The properties specified in the standard for class A1 residential wood pellets include: moisture content of ≤ 10 wt%, ash content of ≤ 0.7 wt% (d.b.), and a maximum of 1.0 wt% of pellets < 3.15 mm in length. In residential combustion, wood pellets are often preferred over wood chips due to higher energy density, lower ash content, and homogeneous quality. Briquettes are manufactured in the same way as pellets, only their size is considerably larger. Briquettes are used in the same way as wood logs in batch combustion devices.

The elementary composition of wood comprises carbon, oxygen, and hydrogen as well as small amounts of nitrogen and other inorganics. Together, these form mainly cellulose ($C_6H_{10}O_5$), constituting about 40–50 % of dry weight depending on the wood species. Other main components are hemicellulose and lignin (Saidur *et al.*, 2011). Cellulose, hemicellulose and lignin are important components of plant cell walls. Generally, hardwood species have more cellulose and hemicellulose, whereas softwood species have more lignin (Alakangas *et al.*, 2016; Grønli *et al.*, 2002; Saidur *et al.*, 2011). The hemicellulose/lignin ratio is known to affect at least the char residue yield (Alén *et al.*, 2002; Zaman *et al.*, 2000), which affects the combustion process—especially in batch-wise combustion. Compared to light fuel oil, wood fuels contain more ash (Kaivosoja *et al.*, 2013; Oasmaa and Czernik, 1999; Sippula *et al.*, 2007). Ash can be present in the biomass either as inherent or extraneous material (e.g. from harvesting or processing the fuel). The inorganic ash components participate in the formation of particle emissions, which is discussed in more detail in Section 3.3.

3.2.2 Alternative fuels

Energy crops can be divided into dedicated energy crops and by-products of field crops. Dedicated energy crops are usually short rotation coppice plantations such as willow or herbaceous biomass like reed canary grass or Miscanthus grass. Field crop by-products in Finland are mostly cereal straw and stems or tops of plants and vegetables (Alakangas *et al.*, 2016). Certain qualities of agricultural fuels are similar when compared to wood fuels. For example, elemental composition and the net calorific value of straw and wood are very analogous, and they both contain a relatively large number of volatiles (Carvalho *et al.*, 2013). Volatile matter in fuel is defined as “components and products releasing from the organic matter in fuel as gas when fuel is heated at 900 °C ± 10 °C for seven minutes in standardised conditions” (Alakangas *et al.*, 2016). The degree of volatility of a compound is measured by its vapour pressure. However, the ash properties of field fuels are usually quite different from wood fuels. Firstly, the ash content in energy crops is significantly higher compared to good quality wood fuels. For example, the ash concentration of wheat straw typically varies between 5 – 9 m-% (from dry weight) (Alakangas *et al.*, 2016; Saidur *et al.*, 2011). Secondly, the melting temperature of ash from field fuel combustion is often remarkably low (Obernberger, 1998; Vassilev *et al.*, 2014). Therefore, combustion of field fuels requires special furnaces and burners designed for combustion of melt-forming fuels (Gilbe *et al.*, 2008; Öhman *et al.*, 2004). In addition to ash melting problems, combustion of energy crops may induce fouling and corrosion problems in heat exchangers and increase emission concentrations (Bankiewicz *et al.*, 2013; Gilbe *et al.*, 2008). These three issues are reliant on the chemistry of the fuel which, for some alternative fuels (e.g. animal biomass, sludge, aquatic biomass), may deviate from wood considerably (Vassilev *et al.*, 2010) (the effect of fuel composition on emissions is discussed further in Section 3.3).

3.3 Influence of fuel raw materials on the applicability of small-scale combustion appliances and combustion emissions

3.3.1 Physicochemical properties of solid biofuels

Both the physical and chemical properties of fuel raw materials have effects on the combustion process and the resultant emissions. Generally, an increase in the moisture content of fuel will decrease the adiabatic combustion temperature because of the energy consumed in the evaporation of water (van Loo and Koppejan, 2008). This temperature decrease may lead to incomplete oxidation of combustion gases and thus increased emissions of incomplete combustion (Nussbaumer, 2003). However, very low moisture content may also increase emissions, especially in conventional batch combustion devices where the increased bed temperature often leads to an elevated fuel devolatilisation rate, which creates excess amount of local oxygen deficiencies (Pettersson *et al.*, 2011). Although in diffusion flames—where oxidizing agent combines with fuel by diffusion—under-stoichiometric combustion zones (local zones where quantitative relationship between oxidizer and fuel is too low) are unavoidable, and in batch combustion devices in particular, the mixing of devolatilisation products with combustion air (the oxidising agent) is usually less than optimal. In addition to the temperature and turbulence (mixing), a sufficient residence time for oxidation reactions is also considered a precondition for complete combustion (Nussbaumer, 2003).

Additionally, moisture content increases the flue gas flow and thus reduces the thermal efficiency of boilers (Alakangas *et al.*, 2016). It has been observed that despite the variations in chemical composition and heating values, the thermal behaviour (i.e. devolatilisation rate as a function of temperature) for different wood species is similar (Grønli *et al.*, 2002). Density of the fuel mainly has an effect on the batch volume, which directly affects the combustion chamber energy input. Fuel porosity can also affect energy input, but the influence of porosity on the reactivity of the fuel is more notable (Cai *et al.*, 1996). Moreover, in small-scale units this is not a matter of concern. Log size can be considered as one of the key factors for optimal combustion in small-scale batch combustion. The effect of batch and log size has been studied by Tissari *et al.* (Tissari *et al.*, 2009) who concluded that too small a log size in closed firebox devices leads not only to a high devolatilisation rate and high emissions of incomplete combustion, but also high particle emissions. Later studies (Nyström *et al.*, 2017; Vicente *et al.*, 2015) have drawn similar conclusions about the importance of correct log size.

The ratio between char and volatiles in fuel affects its reactivity; char is much less reactive than the volatile fraction. Characteristic for batch combustion of biomass is that the hydrogen/carbon (H/C) ratio in fuel decreases towards the end of the batch and the adiabatic combustion temperature increases as a function of the degree of burnout. However, due to the lower reactivity of char (reaction rate is limited by the diffusion of oxygen to the surface of fuel particles) compared to the volatile fraction, less oxygen is consumed at constant combustion air flow during char burning, which means higher excess air ratio. A high excess air ratio and a lower reaction rate reduce the combustion temperature, and thus compensate the higher adiabatic temperature of char burning (van Loo and Koppejan, 2008).

3.3.2 Effects of ash-forming elements and trace metals

Fuel ash content has been shown to affect the combustion conditions and, thereby the combustion emissions. Sippula *et al.* (Sippula *et al.*, 2007) found that a high ash content in wood/bark pellets decreased the burning rate and increased the air-to-fuel ratio in a top-fed pellet stove. In many previous studies on the influence of wood species on combustion emissions, fuel ash has been highlighted as the main determining factor of inorganics in particulate matter (Nyström *et al.*, 2017; Sippula *et al.*, 2007; Wiinikka *et al.*, 2007). Fine particle mass (PM_1) has been also shown to correlate with the amount of fuel inorganics (Sippula *et al.*, 2007). Depending on the fuel composition, the major inorganic compounds formed during wood combustion can be alkali sulphates, chlorides, carbonates, hydroxides and nitrates (Sippula *et al.*, 2007; Wiinikka *et al.*, 2007). Precursors of these compounds vaporise from the hot fuel bed and either create new particles by homogeneous nucleation or condensate on existing seed particles as the flue gas cools down (Jokiniemi *et al.*, 1994) (at a temperature of ~950 °C for sulphates, 650 – 750 °C for some hydroxides, 550 – 600 °C for chlorides and < 600 °C for nitrates and hydroxides). Zinc oxide (ZnO) is found out to often form the seed particle in wood combustion (Torvela *et al.*, 2014). Alkali earth metals are considered non-volatile at small-scale combustion temperatures and they usually remain in the bottom ash (Becidan *et al.*, 2012; Sippula *et al.*, 2007). Nyström *et al.* (Nyström *et al.*, 2017) compared the influence of wood species and burn rate on the emissions of a small-scale batch combustion appliance. In their study, the effect of burn rate on PM emissions was clear—a high burn rate versus a nominal burn rate increased carbonaceous particle emissions. These authors concluded that the influence of wood species on particle emissions was minor; however, they measured more than a two-fold increase in PM_1 emissions for spruce compared to birch. These observations indicate that in batch combustion, it is difficult to harmonise the combustion conditions between tests with different fuels.

The release of alkali metals—the major factor in PM formation in efficient combustion systems—is governed by the inorganic composition of fuel. In particular, the ratios of Si/K, Cl/S and Cl/K are identified as important when determining alkali metal release from the combustion process (Knudsen *et al.*, 2004; Lind *et al.*, 2006; Sippula *et al.*, 2008). The effects of inorganics in fuel are often complex. For example, increased Si or P content decreases the release of alkalis due to formation of alkali silicates/phosphates and thus reduces particle formation, but the formation of alkali silicates often decreases the ash fusion temperature leading to increased slag formation (Gilbe *et al.*, 2008; Sommersacher *et al.*, 2012; Vassilev *et al.*, 2014; Öhman *et al.*, 2004). For silicate-rich biomass ashes, alkali metals (mainly K and Na for biomass) are known to lower the ash fusion temperature, whereas alkaline earth metals (Mg and Ca for biomass) may increase it (Khan *et al.*, 2009; Vassilev *et al.*, 2014).

In addition to increased particle formation, chlorine increases the emissions of hydrogen chloride (HCl) and polychlorinated dibenzodioxins and –furans (PCDD/F) (Obernberger *et al.*, 2006) and may induce high-temperature corrosion (Salmenoja, 2000).

Sulphur can form sulphur dioxide (SO_2) during combustion, which is partly oxidised further into sulphur trioxide (SO_3). SO_3 may then react with alkali chlorides forming alkali sulphates and HCl (Sippula *et al.*, 2008). Thus, in this case, sulphur is providing a protective effect against chlorine-induced high-temperature corrosion. This is capitalised on, for instance, in the co-combustion of biomass and peat (peat has a typically higher sulphur content compared to woody biomass) (Lamberg *et al.*, 2013; Sippula *et al.*, 2017). The downside in this scenario is the increased emission of SO_2 and HCl. Furthermore, if SO_3 is not reacting with alkali chlorides, it may form sulphuric acid, which leads to an enhanced flue gas dew point and potential low-temperature corrosion in boiler plants. Another possibility is that the already deposited alkali chlorides react with SO_2 and form solid potassium sulphate (K_2SO_4), releasing chlorine directly on the surface of the heat exchanger, causing corrosion (Obernberger *et al.*, 1997).

In addition to alkali metals and other ash components, trace metals can also be problematic. This is especially true of lead and zinc, which can be present in notable quantities in recovered fuels, as these are known to form low-melting deposits that cause corrosion. Furthermore, the detrimental health effects of trace metals in aerosols are well known (Järup, 2003). For example, zinc is a typical emission component from combustion of woody biomass that has been shown to induce toxic responses in cell experiments (Uski *et al.*, 2015). Furthermore, ZnO has been noted to act as the first seed particle due to its very low saturation vapour pressure (Torvela *et al.*, 2014). Besides corrosion and emission problems, high levels of trace metals can also hinder the recycling or disposal of ash formed by combustion.

3.3.3 Influence on ash utilisation

The bottom and fly ashes from solid biomass combustion contain considerable amount of plant nutrients but also potentially toxic heavy metals (Wang *et al.*, 2012), which can constrain the utilisation of ashes as fertilisers. In addition to fertilisation, ashes have been utilised for building, embankment filling, as a road base and as a pavement binder (Colonna *et al.*, 2012). When evaluating the suitability of ash as a fertilising agent, it is important to understand the fractionation of species between bottom ash and fly ash particle phases. The limits for fertilisers in Finland (both maximum values for harmful substances and minimum values for nutrients) are specified at a national level by the Ministry of Agriculture and Forestry (Ministry of Agriculture and Forestry of Finland, 2011). Additionally, Directive 2000/76/EC defines limits for trace metals in particulate matter from the incineration or co-incineration of waste (including the sum of Cd + Tl and the sum of Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V) (EC 2000/76).

4 Methods

All the combustion experiments were conducted at the ILMARI combustion research facilities at the FINE (Fine Particle and Aerosol Technology) laboratory, University of Eastern Finland. Particle and gaseous emission components were characterised from continuous combustion of blended solid biomass, continuous combustion of pellets, and batch-wise combustion of wood logs of various species. Elemental analysis of both the fuel samples and the PM_1 filter samples were performed by commercial laboratories.

4.1 Fuels

4.1.1 Wood logs

In **Papers II – IV**, wood logs were combusted in a batch combustion appliance (described in Section 4.2.3). Three wood species were used as fuel: European beech (*Fagus sylvatica*), birch (*Betula pendula* and *Betula pubescens*) and Norway spruce (*Picea abies*). All of these species are common across the northern temperate zone. The beech logs were of German origin, whereas the birch and spruce were from Finland. Fuel samples were taken for the analysis of moisture content, heating value, ash content, and content of common elements (Table 1).

Because of the dynamic nature of the batch combustion process, the repeatability of the experiments is often less than optimal. In order to enhance repeatability, the combustion process was standardised as thoroughly as was deemed appropriate (relative to the day-to-day use). The logs were dried indoors to lower their moisture content (Table 1). After drying, logs were cut to equal length and weight, but the bark was not removed. The combustion process (size and arrangement of logs, ignition, batch duration, etc.) is described in detail in **Paper II**.

Table 1: Chemical composition of fuels.

	Unit	Birch logs	Beech logs	Spruce logs	Pellet	Wood chips (air-staging)	Wood chips (co-combustion)	Reed canary grass	Straw
Study		Papers II – IV	Papers II – IV	Papers II – IV	Paper IV	Paper I	Paper I	Paper I	Paper I
Moisture	wt.%	7.2	9.0	7.4	7.3	18.6	22.4	23.9	10.6
Net calorific value	MJ kg^{-1}*	18.1	17.8	18.6	18.4	18.9	18.8	17.9	17.1
Ash (550 °C)	wt.%*	0.69	1.30	0.58	0.36	$0.6^{\dagger}$	$0.6^{\dagger}$	$2.6^{\dagger}$	$8.0^{\dagger}$
C	wt.%*	51.0	50.3	52.0	51.7	n/a	50.7	48.5	46.1
H	wt.%*	6.0	5.8	5.9	6.0	n/a	6.4	6.2	5.8
O	wt.%*	41.9	42.3	41.1	41.6	n/a	42.0	41.8	34.5
N	mg kg^{-1}*	4000	3600	3600	2900	1700	< 1000	4800	9700
S	mg kg^{-1}*	60	370	90	60	< 200	439	1970	2140
Cl	mg kg^{-1}*	< 50	< 50	50	60	83	30	140	13000
Cr	mg kg^{-1}*	2	5	< 1	< 1	< 1	< 1	1.1	< 1
Cu	mg kg^{-1}*	2	2	1	< 1	1.5	3.5	6.4	4.2
K	mg kg^{-1}*	500	1330	640	380	770	890	1300	30900
Na	mg kg^{-1}*	52	31	11	83	47	63	140	460
Zn	mg kg^{-1}*	33	5	25	14	31	81	48	29

*dry basis; †ash content is calculated based on oxides of ash-forming elements in the fuel: aluminium oxide (Al_2O_3), calcium oxide (CaO), iron oxide (Fe_2O_3), potassium carbonate (K_2CO_3), magnesium oxide (MgO), sodium carbonate (Na_2CO_3), phosphorus pentoxide (P_2O_5), and silicon dioxide (SiO_2)

4.1.2 Wood chips

Wood chips were combusted in experiments described in **Paper I** using a reciprocating step-grate combustion reactor (Section 4.2.1). Wood chips consisted mostly of spruce (70 %), while the rest consisted of typical Finnish deciduous tree species. In air-staging experiments, only wood chips were used as fuel, while in co-combustion experiments wood chips were combusted together with reed canary grass or barley straw. Wood chips were taken from different lots for air-staging experiments and co-combustion experiments, which explains the slight discrepancy in their chemical compositions (Table 1). More detailed results of the fuel analysis are presented in **Paper I**. The supporting information of **Paper I** also features the calculated compositions for fuel mixtures.

4.1.3 Pellets

Pellets were combusted using a pellet boiler as described in Section 4.2.2. The pellets were of commercial quality, manufactured according to ISO 17225-2, the standard for chemically untreated coniferous and deciduous trees containing no bark.

4.1.4 Agricultural fuels

In the co-combustion experiments in **Paper I**, the following two agricultural fuels were co-combusted with wood chips (discussed in Section 4.1.2): (1) spring-harvested reed canary grass (*Phalaris arundinacea*) and (2) autumn-harvested barley straw (*Hordeum vulgare*). Agricultural fuels were prepared with a chaff-cutter to ensure they passed the screw conveyors easily. Before filling the fuel silo (Fig. 1), fuels were mixed manually in a large container and then added in small batches to prevent separation of the fuel types. More detailed characteristics of the agricultural fuels are presented in **Paper I** and its supporting information.

4.2 Combustion appliances

All combustion appliances were grate-fired devices made for solid fuel combustion.

4.2.1 Reciprocating-grate boiler

In **Paper I** the combustion appliance was a 40 kW, multi-fuel, horizontally fed stoker burner equipped with a reciprocating step-grate (Ariterm MultiJet) (Fig. 1) (Leskinen *et al.*, 2014). This design allows the combustion of fuels with high ash content, which are prone to slag formation and would be difficult if not impossible to utilise with a solid grate burner. The nominal capacity of 40 kW generates enough heat for a large detached house, for example. The fuel feed rate, combustion air feed and the low pressure in the combustion chamber were logic controlled. Combustion air was fed in two stages: primary air was fed through the grate and secondary air was fed above the fuel bed. Volumetric flows for primary and secondary combustion air were measured with flow rate sensors (Schmidt Flow Sensor SS 20.60) to calculate the air-to-fuel ratios. Detailed dimensions of the burner and combustion chamber are presented in **Paper I**.

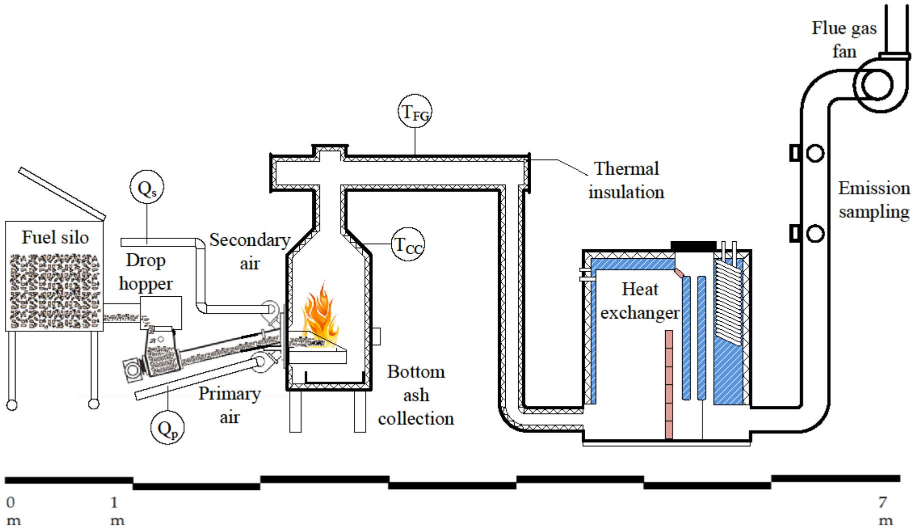

Fig. 1: Schematic of the reciprocating-grate biomass combustion boiler used in the combustion experiments. Q_p and Q_s are primary and secondary air volume flow meters, and T_{CC} and T_{FG} are temperature measurement points in the combustion chamber and flue gas channel, respectively (**Paper I**).

4.2.2 Pellet boiler

The pellet boiler (**Paper IV**) was a fully automated combustion device featuring an integrated burner with a fixed grate (Biotech PZ-RL 25 kW) (Fig. 2) (Lamberg *et al.*, 2011b). The automated functions include the adjustment of the air-to-fuel ratio by controlling the combustion air flows, heat exchanger cleaning, removal and compression of ash, pellet reservoir filling and ignition. The overfed burner had a primary air feed at the bottom of the burner shell and a secondary air feed approximately 10 cm above the grate. Because of the fixed grate, the burner is unsuitable for combustion of melt-forming fuels.

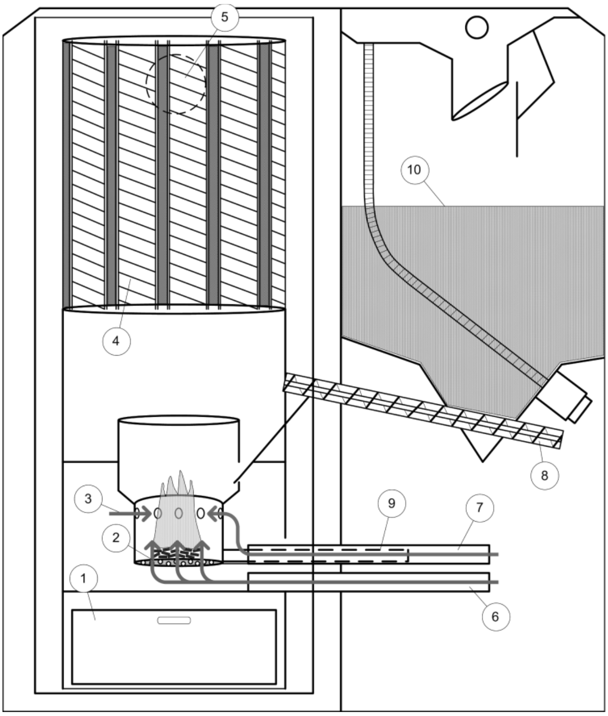

Fig. 2: Schematic of the pellet boiler used in the combustion experiments. 1 ash box, 2 grate and primary air supply, 3 secondary air supply, 4 heat exchanger, 5 flue gas outlet, 6 primary air inlet, 7 secondary air inlet, 8 pellet-feeding screw, 9 ignition fan and 10 pellet storage (Lamberg *et al.*, 2011b).

4.2.3 Logwood-fired masonry heater

A masonry heater was used as the emission source in **Papers II – IV**. The heater was manufactured by Tulikivi Oyj. This device is a so-called modern masonry heater, since the combustion air is divided into separate primary and secondary combustion airs. Compared to more widely used stoves, modern masonry heaters usually feature a heat-retaining structure and a secondary combustion chamber, which enhance combustion and reduce the emissions of incomplete combustion. The structure of a modern masonry heater is presented in Fig. 3. The primary air was fed through the rifts of the grate, below the fuel batch, and the secondary air was fed from the top of the primary combustion chamber, above the fuel batch. Furthermore, the masonry heater featured a specific rack in the combustion chamber for the logs. The purpose of the rack was to lift the fuel batch slightly up from the grate and thus provide less restricted primary air flow, and also to keep the logs close together. A figure of the rack is presented in Supporting Information of **Paper II** (Fig. S1). The flue had a contraflow structure (Fig. 3), where flue gases flow from the upper combustion chamber downwards through the flue gas ducts and finally exit to the chimney from the back of the heater. In this way, the heat contained by the flue gas is retained efficiently in the structure of the heater and is slowly released to the surrounding air.

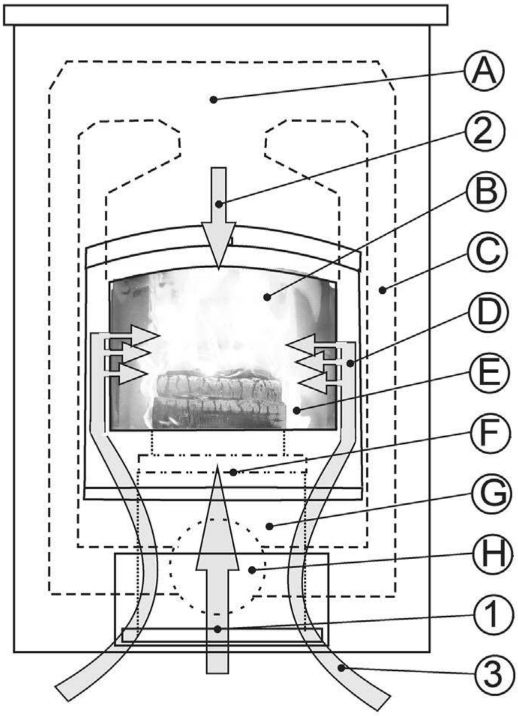

Fig. 3: Schematic of a modern masonry heater used in the experiments. 1 primary air supply, 2 window flushing air supply, 3 secondary air supply, A upper combustion chamber, B secondary combustion zone, C flue gas ducts, D secondary air between ceramic plates, E primary combustion zone, F rift grate, G ash box and H flue gas exhaust to chimney (behind the heater), adapted from (Nuutinen *et al.*, 2014).

Typically, in small-scale batch combustion devices no flue gas fan is utilised. Therefore, the draft (i.e. the low pressure in the stack) is natural and dependent on the structure of the heater flue gas channels, chimney height and predominant weather conditions. In laboratory experiments, the influence of weather conditions and other factors affecting the draft is minimised and so a flue gas fan was utilised. The flue gas fan was attached to the hood, which was placed above the stack (**Paper II** Fig. 1). In this way, the draft was unforced, but could still be precisely controlled. The low pressure in the stack was adjusted to 12.0 ± 0.5 Pa.

4.3 Sampling

Gaseous phase sampling was done directly from the undiluted stack gases, through an insulated and externally heated sampling line (180 °C). Concentrations of oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2) and nitrogen oxides (NO_X) were determined with single-component gas analysers (Magnos 106, Uras 14 and Limas 11 UV; ABB). The concentrations of organic gaseous compounds were measured with a flame ionisation detector (Multi-FID 14, ABB), calibrated against propane. Gaseous compounds were further analysed using Fourier Transform Infrared Spectroscopy (FTIR, DX4000; Gasmet Technologies Oy). The particle emissions were sampled from the stack with a heated sampling probe, featuring a pre-cut cyclone, with a 5 µm cut-off diameter.

4.3.1 Particle sample dilution

It was necessary to dilute the flue gas sample for the online aerosol devices due to high particle number and high mass concentrations. In addition, the high flue gas temperature and moisture content are problematic for most aerosol devices. Dilution is also advantageous with respect to the representativeness of the sample. Diluting quenches chemical and physical processes such as oxidation and coagulation. Furthermore, compared to hot filter sampling of total suspended particles (TSP) (e.g. Environmental Protection Agency Method 5), dilution reduces the sample temperature, which induces condensation of gas-phase semivolatile species on particle phases. Dilutive sampling therefore captures more condensable organic species, which are mainly formed during incomplete combustion, and can give a more realistic overview of the PM emissions than hot sampling. In this work, all the particle samples were taken from the stack with a diluting sampling system, which consisted of an externally heated sampling probe, a porous tube diluter (PRD) and an ejector diluter (ED) (Lyyränen *et al.*, 2004; Tissari *et al.*, 2007). The probe was heated to 250 °C to prevent the condensation of volatile components before diluting the sample. In all experiments, sample dilution was performed either in two or in three stages. Primary dilution was always done with a PRD, while secondary (and possible tertiary) dilutions were done with an ED. The advantage of PRDs is lower particle loss, whereas EDs ensure good mixing of the sample.

The dilution ratio was defined against CO_2 concentrations before and after dilution:

$$DR = \frac{CO_{2,FG} - CO_{2,BG}}{CO_{2,D} - CO_{2,BG}} \tag{4.1}$$

where $CO_{2,FG}$ is the CO_2 concentration of undiluted flue gas; $CO_{2,BG}$ is the approximate concentration in the dilution air; and $CO_{2,D}$ is the concentration in the diluted sample gas stream (Lipsky and Robinson, 2006). A typical dilution ratio after two-stage dilution was between 1:40 and 1:100, and 1:400 after a third stage.

For experiments in **Paper I**, the dilution air consisted of filtered, particle-free and dry pressurised air. In **Papers II – IV**, dilution air was additionally purified with a zero air generator (737-15, AADCO Instruments Inc.). The dilution airflows to the PRD and the ED were controlled with mass flow controllers to ensure stable dilution factors.

Normalisation was performed for the gaseous and particulate emissions according to the Finnish standard on stationary source emissions (SFS5624; Reda *et al.*, 2015). The emissions from all combustion devices were normalised to mg MJ^{-1} in dry flue gas at 0 °C.

4.3.2 Filter sampling and analyses

Before each filter, a pre-cut impactor (Dekati PM10) was used to remove particles larger than 1 μm in aerodynamic size. The collection plates of the impactor were coated with Apiezon-L grease to increase the adhesion of the particles and to reduce the particle bounce. The inorganic composition of PM_1 was analysed from samples collected on 47 mm PTFE filters (offline analysis is described in Section 4.4.1). Filter samples were also analysed gravimetrically with a microbalance (Mettler Toledo MT5) to an accuracy of 1 μg. Finally, the concentrations of organic carbon (OC) and elemental carbon (EC) were analysed from quartz fibre filters with a Carbon Aerosol Analyser (Sunset Laboratory, Inc.) utilising the thermal-optical method, according to the National Institute for Occupational Safety and Health protocol 5040 (NIOSH, 1999).

4.3.3 Gas-phase carbonyls

Gas-phase carbonyl samples (aldehydes and ketones) in **Paper IV** were taken from the diluted and particle-free (filtered with quartz fibre filter) flue gas stream using 2,4-dinitrophenylhydrazine (DNPH) cartridges. Cartridges (Sigma Aldrich, ORBO™ 555) contained silica gel adsorbent coated with 300 mg of DNPH in the front section and 150 mg in the back section. The back section served as a back-up in case of any breakthrough due to the high sample concentrations. Thereafter, the samples entered the cartridge, where carbonyls reacted with DNPH forming hydrazones, which remained captured in the cartridge. After sampling, cartridges were capped and stored at 5 °C. Carbonyls were analysed from the cartridges with selective ion monitoring gas chromatography-mass spectrometry (GC-SIM-MS).

4.4 Chemical characterisation of emissions

4.4.1 Offline analysis

Filter samples described in Section 4.3.2 were analysed with inductively coupled plasma mass spectroscopy (ICP-MS) for concentrations of Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, Tl, U, V and Zn ($HF-HNO_3$ dissolution) and with ion chromatography (IC) for anion concentrations (Br^-, Cl^-, F^-, SO_4^{2-}, NO_3^- and PO_4^{3-}) (with water dissolution). Both the ICP-MS and IC analyses were performed by a commercial analysis laboratory.

4.4.2 Online analysis

Particle chemical composition was measured online with a Soot Particle High Resolution Time-of-Flight Aerosol Mass Spectrometer (SP-AMS; Aerodyne Research, Inc.) (Onasch *et al.*, 2012) (**Paper II**). The SP-AMS utilises a laser vaporiser in addition to a tungsten vaporiser for quantification of the refractory components. In this study, dual and single vaporiser modes were alternated every 60 seconds. This ensured that both the refractory and non-refractory species could be quantified. The sample was ionized with electron ionization (EI), where a beam of electrons collides with sample molecule, resulting in removal of electron from sample molecule, producing a positively charged ion (or rather often cation and radical fragments). After ionisation, m/z of the analytes was measured with a time-of-flight type mass spectrometer.

Volatile and semivolatile organic compounds from batch combustion of wood were measured with Single Photon Ionisation Time-of-Flight Mass Spectrometry (SPI-TOFMS) (TOFMS; Compact Reflectron Time-of-Flight Spectrometer II, Stefan Kaesdorf Geräte für Forschung and Industrie) (Diab *et al.*, 2015) (**Paper III**). Ionization was done by photons generated by Nd:YAG laser (Spitlight 400, Innolas GmbH). For the SPI-TOFMS the samples were not diluted, but filtered (to separate particulate matter) with a quartz fibre filter heated to 230 °C to prevent condensation. The SPI technique utilises ultraviolet photons in vacuum for soft ionisation of gaseous molecules. The advantage of the soft ionisation method is that it causes little or no fragmentation of produced molecular ions compared to hard ionisation methods like EI. Less fragmentation of the generated ions makes data interpretation more straightforward (Adam and Zimmermann, 2007; Mühlberger *et al.*, 2005). The wavelength of the photons was 118 nm, which compares to an energy of 10.49 eV, thus compounds with an ionisation energy below this could be ionised and analysed with SPI-TOFMS.

4.5 Physical characterisation of particulate emissions

The particle number size distributions were measured with a Scanning Mobility Particle Sizer (SMPS, TSI) (Wang and Flagan, 1990) and an Electrical Low Pressure Impactor (ELPI, Dekati) (Keskinen *et al.*, 1992). The SMPS consisted of an electrostatic classifier (Model 3080L, TSI) and a Condensation Particle Counter (CPC Model 3775, TSI) (McMurry, 2000) with a flow rate of 0.3 litre per minute (lpm). The classifier first charges and then classifies the charged particles according to their electrical mobility with a Differential Mobility Analyser (DMA Model 3081, TSI), after which particles are detected optically with CPC. CPC operates by drawing the aerosol sample through alcohol vapour into a cooled condenser, at which point the supersaturated alcohol vapour condenses onto the surface of the particles, enlarging them so that they become optically detectable. The resolution (and the size range) of the SMPS is limited by the scan time (the voltage scan rate of the central electrode high voltage). In batch combustion, changes occur more rapidly than during continuous combustion, and thus, an up-scan time of only 30 seconds was used, giving the size range of ~25 nm to ~390 nm. In continuous combustion of pellets and wood chips, the up-scan time was increased to 120 seconds, which gave the size range of ~14 nm to ~690 nm and a higher size resolution.

The ELPI classifies particles like a normal low pressure cascade impactor, according to their aerodynamic diameter (7 nm - 10 µm). Large particles (D50 % 6.3 µm in aerodynamic diameter, D50 % is a statistical value that denotes a particle size from which half gets collected and half gets cut-off) are cut off at the inlet as they are not able to follow the gas stream due to their inertia. The next impactor stage collects slightly smaller particles (D50 % ~3.8 µm aerodynamic diameter) and so on. As a filter stage was utilised, the smallest particle size assessed was ~7 nm (computational). The particles are charged with a unipolar corona charger before they enter the impactor. They are detected with electrometers based on the charge they carry. The ELPI had vacuum oil embedded sintered collection plates to reduce particle bounce, and it was operated with the filter stage and a flow rate of 10 lpm.

In **Paper I**, particles from the co-combustion of wood and straw were analysed with Transmission Electron Microscopy (TEM, JEOL JEM 2100F FEG/STEM) and energy-dispersive X-ray spectroscopy (EDS), using the scanning mode of the TEM. Furthermore, phase composition of the particle samples was analysed with an X-ray diffractometer (XRD, D8 Discover, Bruker). The operating principle of a TEM is similar to traditional optical microscopy; however, TEM imaging is based on the absorption and scattering of an electron beam instead of visible light. The resolution of optical microscopy is limited by the wavelength of light, while the wavelengths used in TEM are considerably shorter and thus the resolution is significantly higher (~0.2 nm). The wavelength of radiation in TEM depends on the acceleration voltage of the electrons (typically in the order of 70 kV, which gives a wavelength of 4.5×10^{-6} µm (Hinds, 1999). EDS was used for chemical characterisation of the sample. The operating principle of EDS is to focus a beam of electrons or X-rays into the sample, which ejects inner shell electrons of the specimen's atoms creating an electron hole in the inner shell. This hole is filled by electrons from the outer shell, which releases energy in a form of characteristic X-rays. The specimen is identified by the acquired X-ray spectrum. XRD analysis is founded on the scattering of X-ray waves by the atoms of the specimen. If the structure of the specimen material is crystalline, the scattered waves form a diffraction pattern following Bragg's law:

$$2d \sin \theta = n\lambda, \tag{4.2}$$

where d is the distance between adjacent diffracting planes; θ is the scattering angle; n is positive integer; and λ is the wavelength of the beam. Based on these methods, it was possible to identify the morphology, chemical composition and phase composition for the particle samples.

In **Paper II**, the total surface area of particulate matter was analysed with a Nanoparticle Surface Area Monitor (NSAM 3550, TSI). The operating principle of the NSAM is to charge the sampled particles and then detect the charge using an electrometer (Shin *et al.*, 2007). The charge is known to be directly related to the particle surface area. The NSAM takes a sample flow of 2.5 lpm and splits it into a 1.5 lpm aerosol flow and a 1 lpm side flow, which is filtered free from VOCs and particles. This filtered side flow is then ionised and mixed again with aerosol flow, leading to the charging of the particles (diffusion charging). Finally, the charge is detected at the electrometer (inside a Faraday cage) and converted to particle surface area. By default, the NSAM is set to sample one of two deposition fractions, tracheobronchial or alveolar, as selected by the operator using pre-set trap voltages. The deposition fractions for each particle size are defined by the ICRP model (Asbach *et al.*, 2009). In this study, the NSAM was utilised in a custom response mode using the smallest possible trap voltage (20 V) with no ions reaching the Faraday cage, the aim of this method was to measure the total surface area of particles in the size range of 20 to ~400 nm (Asbach *et al.* 2009). The calibration factor was unity.

In addition to filter sampling, particle mass emission was measured online with a Tapered Element Oscillating Microbalance (TEOM 1405, Thermo Scientific) (Patashnick and Rupprecht, 1991). The TEOM consisted of a filter cartridge on top of an oscillating hollow glass tube (tapered element), enclosed in a heated sampling unit. Aerosol sample is drawn through the filter with a vacuum pump at a constant flow rate regulated with a mass flow controller. As particle mass is collected on the filter, the vibration frequency of the tapered element decreases (due to increased inertia) and the accumulated mass can be calculated from the change in frequency:

$$dm = K_0 \frac{1}{f_1^2} - \frac{1}{f_0^2} \tag{4.3}$$

where dm is change in mass; K_0 is spring constant; and f_0 and f_1 are initial and final frequencies, respectively.

5 Results and discussion

5.1 Influence of fuel type on combustion emissions

In general, fuel type had the greatest impact on the mass of particle emissions (Table 2) whereas the type of combustion appliance mostly affected the gaseous organic emissions (Table 3). Orasche et al. (2012) investigated small-scale wood combustion and their study shows similar outcome. In batch-wise combustion, hardwood species produced the highest total PM_1 emissions. In addition, the proportion of the elemental carbon from total PM_1 mass was highest for the hardwood species (average EC values were ~75 % of the PM_1 mass for hardwoods and ~50 % for softwood), while the proportion of organic carbon was comparable between the wood species.

In continuous combustion, the optimised combustion of pure wood fuels (i.e. wood chips and softwood pellets) produced relatively low emissions of both particulate and gaseous compounds.

For co-combustion of wood chips and agricultural fuels, the reed canary grass co-combustion produced only slightly higher emissions compared to pure wood chip combustion (e.g. PM_1: 12.1 mg MJ^{-1} for wood chips, 20.1 mg MJ^{-1} for wood chips and RCG). However, the co-combustion of wood chips with straw was found to produce considerably higher emissions of particulate matter (PM_1: 167 mg MJ^{-1}). Both agricultural fuels contained high amounts of ash compared to pure wood (especially Si, K, Na and P). In addition to the total content of ash-forming elements, the agricultural fuels also contained high amounts of certain components related to elevated emissions and potential corrosion problems (N, S and Cl; Table 1). Among the studied biomass types, further analysis of fuel molar ratios $(Si + P + K)/(Ca + Mg)$ (Sommersacher *et al.*, 2012) predicted that the agricultural fuels would have the lowest ash fusion temperatures. Accordingly, the measured ash fusion temperatures were lowest for straw (Appendix 1: Table 5). Reed canary grass had a slightly higher ash fusion temperature and it was found to cause fewer operational problems than straw, since straw induced clear slag formation on the grate. The formation of slag can potentially cause increased emissions due to plugging of the fuel feed or the air supply, or via other kinds of interference with the combustion reaction (Baxter *et al.*, 1998).

Table 2: Average emission factors for particulate matter and main gaseous components and their standard deviations (in dry flue gas).

		PM$_1$ (mg MJ^{-1})	**PM$_1$ OC (mg MJ^{-1})**	**PM$_1$ EC (mg MJ^{-1})**	**N_{ELPI} (MJ^{-1})**	**CO (mg MJ^{-1})**	**NO$_X$ (mg MJ^{-1})**
Batch combustion	**Birch**	89.9 ± 7.3	3.2	67.5	8.99E+13 ± 1.50E+14	1622 ± 2654	102 ± 32
	Beech	65.4 ± 0.4	3.6	49.8	9.98E+13 ± 9.54E+13	1226 ± 1814	112 ± 40
	Spruce	28.6 ± 2.7	2.4	15.2	6.93E+13 ± 1.23E+14	1837 ± 3431	84 ± 23
Continuous combustion	**Wood chips 1**	12.1 ± 0.8	0.0 ± 0.0	0.0 ± 0.0	1.4E+13 ± 1.5E+12	2.1 ± 1.6	179 ± 11
	Wood chips 2	14.1 ± 2.3	0.2 ± 0.2	1.0 ± 0.9	1.6E+13 ± 5.2E+12	64 ± 200	158 ± 20
	Wood chips 3	22.8 ± 2.4	0.7 ± 0.1	6.5 ± 1.5	1.7E+13 ± 8.3E+12	146 ± 217	124 ± 16
	Wood chips 4	213 ± 100	72 ± 43	73 ± 34	2.4E+13 ± 1.3E+13	982 ± 993	n/a
	Wood chips + reed canary grass (78/22)	20.1 ± 3.9	0.4 ± 0.1	0.0 ± 0.0	3.2E+13 ± 2.1E+12	9.6 ± 3.1	212 ± 17
	Wood chips + straw (67/33)	213	0.7	2.4	3.20E+12 ± 7.7E+12	408 ± 642	158 ± 61
	Wood chips + straw (78/22)	167	1.0	16	1.4E+12 ± 4.1E+12	211 ± 465	216 ± 57
	Softwood pellets (optimal combustion)	16.0 ± 2.0	0.4 ± 0.1	0.5 ± 0.3	4.6E+13	42	92
	Softwood pellets (non-optimal combustion)	17.8 ± 2.4	3.6	6.4 ± 1.3	5.5E+13	230	85

n/a = not available

Table 3: Emission factors for selected organic compounds (in dry flue gas).

		Organic Gaseous Compounds (mgC MJ^{-1})	**Propene (µg MJ^{-1})**	**Butadiene (µg MJ^{-1})**	**Benzene (µg MJ^{-1})**	**Toluene (µg MJ^{-1})**	**Naphthalene (µg MJ^{-1})**	**Styrene (µg MJ^{-1})**	**Formaldehyde (µg MJ^{-1})**	**Acetaldehyde (µg MJ^{-1})**	**Propanal (µg MJ^{-1})**
Batch combustion	**Birch**	16	647	189	814	134	189	51	3638	1202	204
	Beech	34	1318	228	1352	163	270	65	6301	2153	382
	Spruce	20	1073	295	1202	236	279	70	5794	2071	290
Continuous combustion	**Wood chips + reed canary grass (78/22)**	1.3	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Wood chips + straw (67/33)	3.4	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Wood chips + straw (78/22)	3.0	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Softwood pellets (optimal combustion)	1.5	37†	16†	23†	7†	10†	4†	169	71	16
	Softwood pellets (non-optimal combustion)	2.1	55†	31†	215†	18†	70†	11†	185	92	16

n/a = not available; †(Czech *et al.*, 2017)

5.2 Emission factors

5.2.1 Gaseous emissions

In logwood combustion, the emission factors for CO were similar to those observed for batch combustion devices equipped with air-staging (Lamberg *et al.*, 2011a; Nuutinen *et al.*, 2014). The differences observed between the wood species were not substantial for CO emissions. For all species, the ignition batch had moderate CO emissions (ranging from 1680 mg MJ^{-1} to 1990 mg MJ^{-1}) (exceeding the average emission), the intervening batches (batches 2 – 6) had low CO (lowest batch averages were below 450 mg MJ^{-1} for all species), and the burnout phase always produced considerably higher CO emissions (highest 8960 mg MJ^{-1} for spruce, lowest 3370 mg MJ^{-1} for beech). The high ignition phase CO was concluded to result from the cold conditions in combustion chamber, leading to incomplete combustion. As the temperature increased, the oxidation of combustion products became more efficient and CO emissions decreased. The high CO during the burnout phase was likely due to accumulated char bed on the grate. Char accumulation was particularly notable for spruce, which had the highest CO emissions during the burnout phase. The air-staging in batch combustion devices is known to decrease overall CO, but also to potentially increase CO during the burnout phase due to decreased air flow through the grate, allowing the char bed to accumulate during the stable combustion (Nuutinen *et al.*, 2014). During the char burnout phase, the combustion rate is limited by the diffusion of oxygen onto the fuel particles, and this is why CO emissions are generally high during this phase. In continuous combustion, CO emissions were highly dependent on combustion air flow ratios (i.e. the degree of optimisation). The optimised combustion of pure wood fuels (Table 2; wood chips 1 and softwood pellets) produced very low CO emissions, as expected. However, the co-combustion of wood chips with reed canary grass also produced remarkably low CO emissions. In comparison, the non-optimised combustion of good quality fuels produced CO emissions up to one order of magnitude higher than with optimal combustion. In addition, the co-combustion of wood chips with straw resulted in reduced combustion quality and higher emission of CO. The quality of straw co-combustion was slightly improved by reducing the share of straw from 33 wt-% to 22 wt-%.

Emission of organic gaseous compounds (OGC) results from wood pyrolysis and incomplete conversion of these pyrolysis products to CO_2 and H_2O. Possible reasons for this include a too low temperature, too short a residence time, or inefficient mixing of pyrolysis gases and air. At least one of these conditions is often met in batch combustion devices, which is why these devices have high OGC emissions compared to continuous combustion devices. In this study, batch combustion produced OGC emissions one order of magnitude higher than continuous combustion. However, compared to other studies (Nuutinen *et al.*, 2014; Orasche *et al.*, 2012), the batch combustion OGC emissions measured in this study can be considered relatively low (Table 4). In batch combustion, OGC emissions seemed to be strongly dependent on the combustion temperature. Therefore, the OGC emissions were always highest for the ignition batch; temperature was too low for efficient secondary combustion.

Formaldehyde and acetaldehyde were the major carbonyl compounds (with average contributions of 58 % and 19 % for birch, 63 % and 21 % for beech and 64 % and 22 % for spruce, 53 % and 23 % for softwood pellets, respectively of total carbonyl compounds (CC's)) in the emissions for all of the wood species, regardless of the combustion appliance. The emission factors of CCs were highest for the combustion of spruce and beech, and lowest for birch. The ignition phase always produced the highest CC concentrations. The emission factors for batch-wise combustion were considerably lower (2 – 15 times) than those reported in previous studies conducted with batch combustion devices (Cerqueira *et al.*, 2013; Evtyugina *et al.*, 2014; Hedberg *et al.*, 2002; Schauer *et al.*, 2001). Furthermore, the CC emissions from pellet combustion were approximately 20 times lower than those measured for the batch combustion device. No significant increase in CC emissions was observed for non-optimised combustion of pellets.

Unlike CO and hydrocarbons, emissions of NO_X are not considered as emissions of incomplete combustion—on the contrary, they usually peak during efficient combustion (if no primary or secondary NO_X abatement is applied) (Eskilsson *et al.*, 2004). In this study, NO_X emissions were primarily dependent on the amount of fuel nitrogen and its conversion rate to NO_X, which depends on the combustion technology and efficiency. In small-scale combustion, temperatures are considered too low for thermal NO_X formation. Even though all combustion devices had a staged combustion air feed, none of them were designed for NO_X reduction. The combustion of agricultural fuels produced the highest NO_X emissions. The fuel N content was especially high for straw (9700 mg kg^{-1} in straw vs <1000 mg kg^{-1} in wood), and this is why straw combustion produced high NO_X despite otherwise low combustion quality (average NO_X emissions for wood + straw were 158 mg MJ^{-1} or 216 mg MJ^{-1}, depending on the fuel mixing ratio). The fuel N content of reed canary grass was almost exactly half that of straw, but NO_X emissions were about the same (averaging 212 mg MJ^{-1} for wood + reed canary grass). This is explained by the higher combustion efficiency of reed canary grass and thus a higher nitrogen conversion rate. Also, the fuel N conversion rate to NO_X has been shown to be higher for fuels with low nitrogen content compared to fuels with high N content (Díaz-Ramírez *et al.*, 2014; Houshfar *et al.*, 2012). For continuous combustion, the pellet combustion emitted the lowest NO_X emissions (averaging 92 mg MJ^{-1} during optimal combustion) even though the pellets had a higher N content than wood chips. Batch combustion fuels had no large differences regarding N content. Differences in NO_X emissions were mostly due to combustion conditions. For example, beech combustion had the highest average air-to-fuel ratio (averaging 5.2) and produced the highest NO_X emissions (averaging 112 mg MJ^{-1}), probably due to more efficient N oxidation compared to the combustion of birch or spruce. Overall, average NO_X emissions were similar between the fuel types and between the combustion devices (Table 2).

Emissions of SO_2 or HCl are usually negligible in small-scale wood combustion and thus do not pose a problem. However, the contents of sulphur and chloride in agricultural fuels studied in **Paper I** were significantly higher compared to wood fuels (Table 1). This led to increased emissions of SO_2 and HCl in the combustion of reed canary grass and straw (**Paper I**: Table 3). In addition, high sulphur emissions may induce low-temperature corrosion in boilers. Furthermore, SO_2 and HCl emissions can participate in acid precipitation (van Loo and Koppejan, 2008).

5.2.2 Particle emissions

For batch-wise combustion, the differences in PM_1 emissions were exceptionally high (Table 2). The lowest mass emission was measured for spruce combustion (averaging 28.6 mg MJ^{-1}) and the highest was for birch combustion (averaging 89.9 mg MJ^{-1}), a difference of more than three times.

Compared to previous batch combustion studies, the average mass emissions of beech and birch were similar (Nuutinen *et al.*, 2014; Orasche *et al.*, 2012; Tissari *et al.*, 2008a); however, the mass emission from spruce combustion was clearly lower than in previous studies (Nyström *et al.*, 2017; Orasche *et al.*, 2012). The PM_1 emission of spruce was not much higher than from the continuous combustion of pellets or co-combustion of reed canary grass.

The optimised combustion of wood chips produced the lowest PM_1 emissions (12.1 mg MJ^{-1}). The co-combustion of reed canary grass or combustion of pellets produced only slightly higher mass emissions. However, the co-combustion of straw produced significantly higher PM_1 emissions—more than double that of batch combustion of birch logs. Emission was so high that, in daily operation, it would probably cause severe heat exchanger fouling and, consequently, efficient particle filtration or removal method would be advisable in addition to automated heat exchanger cleaning.

The vast majority of the particles (in terms of number) from all combustion scenarios were submicron particles (< 1 µm in aerodynamic diameter). The average particle number concentration was highest for the batch combustion of logwoods. The continuous combustion of pellets and the batch combustion of logwoods produced the smallest average particle size, with a geometric mean diameter (GMD) of < 70 nm as measured by ELPI (GMD_{ELPI}). The measured GMDs are in line with previous publications (Lamberg *et al.*, 2013; Lamberg *et al.*, 2011a). No significant differences were observed between wood species in batch-wise combustion. The non-optimised combustion of pellets produced a GMD_{ELPI} similar to co-combustion of wood chips and reed canary grass (< 80 nm). The optimal combustion of pure wood chips produced slightly larger particles (~100 nm) and the co-combustion of wood chips with straw produced notably larger particles (GMD_{ELPI} > 400 nm). Additionally, particles from straw combustion were analysed in detail with TEM, EDS and XRD (**Paper II**: Fig. 6). The analyses revealed that particles were mainly formed of crystalline potassium chloride (KCl). This deviates significantly from the typical amorphous, often agglomerated particles resulting from pure wood combustion (Torvela *et al.*, 2014).

When comparing the agricultural fuels, straw combustion produced a lower number of particles than reed canary grass. However, the GMD from straw combustion was considerably larger. The high number of particle emission from reed canary grass combustion was probably due to a high Zn concentration in this fuel. ZnO acts as a seed particle, on which inorganic and organic materials condense. In comparison, straw had a high Cl concentration, which likely led to the formation of zinc chloride ($ZnCl_2$) and KCl. Both of these compounds have relatively high vapour pressure and thus are unlikely to form new particles, but rather tend to condense on existing particles. This is one factor that leads to the low number emissions and a high GMD from straw co-combustion.

5.2.2.1 Organic and elemental carbon

Organic carbon (among others) is considered as emission of incomplete combustion, and these types of emissions were substantially affected by the combustion air distribution. With elemental carbon, the effect of air-staging is less straightforward, as it has been shown to potentially either decrease or increase EC emissions (Nuutinen *et al.*, 2014). In this study, an effect on EC emission was notable, particularly during continuous combustion (**Paper I**: Fig. 2). In optimised continuous combustion, average emissions of OC and EC were negligible compared to batch-wise combustion (e.g. EC emissions: < 0.0 mg MJ^{-1} for wood chip + reed canary grass co-combustion vs. 49.8 mg MJ^{-1} for batch combustion of beech). This has also been shown in numerous other studies (Lamberg *et al.*, 2011a; Tissari *et al.*, 2008a). Conventional batch combustion devices are especially known to have high organic emissions (Nuutinen *et al.*, 2014; Tissari *et al.*, 2009). In batch combustion, EC emissions were affected by the fuel type. Birch combustion clearly produced the highest average EC emissions and spruce combustion produced the lowest. EC emissions from both birch and spruce decreased as the rate of combustion increased (verified by low lambda values during the stable combustion phase). With beech wood, no clear trend was observed, although for all species the char-burning phase produced the lowest average EC emissions. Nuutinen *et al.* (2014) proposed that the air-staging in batch combustion may increase EC emissions in some circumstances, because of the cooling effect of secondary air.

The addition of reed canary grass to wood chips increased OC emissions only slightly compared to pure wood chip combustion; the addition of straw to wood chips substantially increased EC emissions.

5.2.3 Comparison to earlier studies

Table 4: Comparison of main emission components from batch combustion of wood.

Study	Emission (mg MJ^{-1})	Spruce	Beech	Birch
This study	OGC	20	34	16
Orasche *et al.* 2012		155	162	-
Nuutinen *et al.* 2014		-	-	96
This study	CO	1837	1226	1622
Orasche *et al.* 2012		1940	1850	-
Nuutinen *et al.* 2014		-	-	1112
This study	NO_X	84	112	102
Orasche *et al.* 2012		88	145	-
Nuutinen *et al.* 2014		-	-	-
This study	PM_1	28.6	65.4	89.9
Orasche *et al.* 2012		67	93	-
Nuutinen *et al.* 2014		-	-	40.2
This study	PM_1 EC	15.2	49.8	67.5
Orasche *et al.* 2012		9.3	41	-
Nuutinen *et al.* 2014		-	-	23.9
This study	PM_1 OC	2.4	3.6	3.2
Orasche *et al.* 2012		11	15	-
Nuutinen *et al.* 2014		-	-	18.8

Reviewing the average emission values from small-scale batch combustion of wood from this study and two earlier similar studies (Table 4) confirms that different wood species can have different combustion emissions. In this study and Nuutinen *et al.* (2014), the combustion appliance was heat-retaining masonry heater and in study by Orasche *et al.* (2012) the appliance was a log wood stove.

In above mentioned studies, gaseous organic emissions seems to be lowest for birch and highest for beech, while NO_X emissions are lowest for spruce. However, in many studies with various wood species the conditions or combustion appliances have so many dissimilarities that straight comparison is not reasonable. In this study the average fine particulate mass emission was clearly highest for birch (89.9 mg MJ-^{1}) and most of the mass was elemental carbon (67.5 mg MJ^{-1}). However, Nuutinen *et al.* (2014) measured only 40.2 mg MJ^{-1} of PM_1 from birch combustion and a smaller proportion of EC (75 % vs. 59 %). On the contrary, in this study the proportion of OC in PM_1 was small (< 8 %) but in Nuutinen et al. (2014) it was ~47 %. This shows that the appliance has a considerable effect not only on the mass emission but also on the composition of emission.

5.3 Time-resolved emissions during batch combustion of wood

5.3.1 Gaseous emissions

The temporal variation of CO emissions was typical for devices with a staged combustion air feed; the emissions were high at the ignition phase (1st batch), low during the stable combustion phase (batches 2 to 6) and high again at the char-burning phase. Deviations in CO emissions were minor between the wood species during stable combustion. However, differences during the char-burning phase were significant; beech combustion produced the least CO during the char-burning phase, which was on average half that of spruce.

5.3.1.1 Organic gaseous compounds

Emission of organic gaseous compounds was highest at the ignition phase (from a cold start) or immediately after the addition of a new batch to the glowing char bed. The combustion of birch logs, in particular, produced high OGC peaks (**Paper II**: Fig. 5). These high emissions were probably a result of insufficient temperature and thus inefficient secondary combustion. During the char-burning phase, OGC emissions were observed to increase. This was mostly methane, which is known to form in char gasification reactions (Eq. 5.1 – 5.3) (Kleinhans *et al.*, 2017).

$$C + CO_2 \rightarrow 2CO \tag{5.1}$$

$$C + H_2O \rightarrow CO + H_2 \tag{5.2}$$

$$C + 2\,H_2 \rightarrow CH_4 \tag{5.3}$$

The time-resolved emission of OGCs highlighted the importance of the ignition phase; slow ignition increased the emission considerably (**Paper III**). OGC emissions were typically highest during the first two batches. For example, 51–63 % of the total benzene emission was released during the first batch (**Paper III**). According to the literature, the release of benzene is not typical at temperatures under 900 K for wood fuels (Nowakowska *et al.*, 2014). In this study, benzene was likely formed by pyrosynthesis. Furthermore, naphthalene was observed to have a high correlation with benzene, presumably due to the same formation mechanism.

5.3.2 Particle emissions

Particle mass emissions measured by TEOM were typically highest either after the insertion of a new batch or during the most intense burning phase (**Paper II**: Supplementary Fig. 3).

However, there were some differences between the wood species in the formation of mass emissions; beech produced the highest emissions during the final third of a batch, whereas birch had two clear emission peaks per batch—one at the beginning and the other (similar to beech) towards the end of a batch. Spruce had considerably lower average mass emission compared to the hardwood species. There were also clear peaks during the first two batches of spruce combustion, after which emissions stabilised considerably. Common to all these cases, peaks in mass emissions were all attributed to the increased formation of refractory black carbon (rBC) (**Paper II**: Fig. 7).

The temporal variation of particle number and surface area concentrations followed the mass concentration closely (**Paper II**: Fig. 2 and Supplementary Fig. 4). The surface area and number concentrations were highest immediately after the insertion of a new batch. These peaks at the beginning of each batch were, however, very brief. Typically, another peak in number and surface area concentrations was observed during the most intense burning phase. The surface area concentration for birch combustion was lowest during the char-burning phase. For spruce, no such clear distinction between combustion phases (based on surface area concentration) was seen.

The temporal variation in GMD was notably different between the wood species (Fig. 4). For birch, the GMD was highest during the stable burning phase of each batch (considered to start after ~3 minutes from batch insertion on glowing char bed) and dropped notably during the char-burning phase (the last ~5 minutes of each batch and the whole 7th batch). For beech combustion, the GMD was low at the beginning of a batch and increased towards the end of batch until the char-burning phase, when the GMD was lowest. For spruce, a high amount of char residue produced particles with considerably lower GMD (~50 nm).

5.3.2.1 Organic aerosols

The mass concentration of organic aerosols (OAs) measured by AMS was highest for beech and birch. For beech, the highest OA emissions were produced at ignition (Fig. 5). The ignition of beech was typically slower compared to birch or spruce; this type of ignition is more prone to causing higher emission of organics due to a longer cold period compared to fast ignition. The effect of ignition on organic emissions has been acknowledged also in earlier studies (Tiitta *et al.*, 2016). For birch combustion, the addition of a new batch typically produced a high momentary concentration of OAs. Unfortunately, these peaks were not captured in, for example, the AMS spectrum illustrated in Fig. 5 due to the alternating PTOF (Particle Time-of-Flight) mode, which led to reduced time resolution (operated for 20 s per minute). The time-resolved OA emissions of spruce were quite different compared to hardwood combustion; OA emissions increased towards the end of a batch, and were highest during the final char-burning phase. For beech and birch, OA concentrations decreased as the combustion chamber temperature increased, when secondary combustion was enhanced. Notably, in the case of birch combustion, the volatility of OAs was found to increase rapidly at the end of the flaming phase and when char burning was initiated. This led to a decrease in this emission of particulate organics and an increase in the emission of gaseous organics.

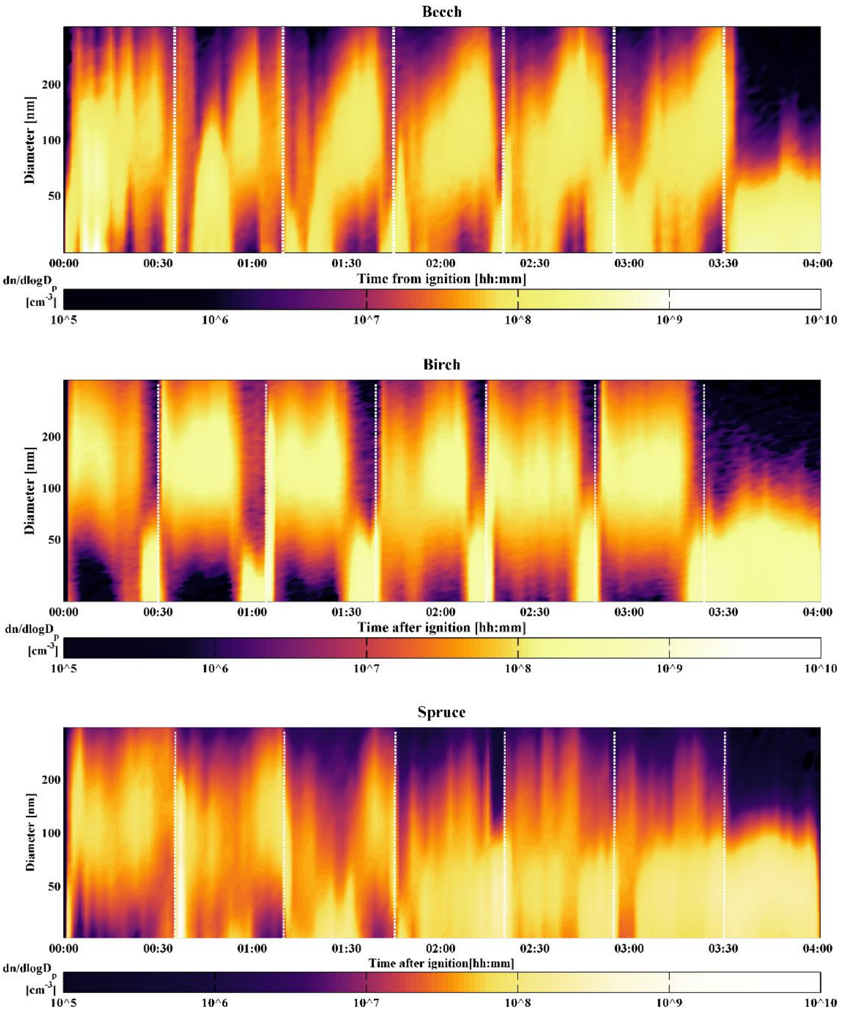

Fig. 4: Number size distribution for the batch combustion of beech, birch and spruce, measured by a Scanning Mobility Particle Sizer (SMPS).

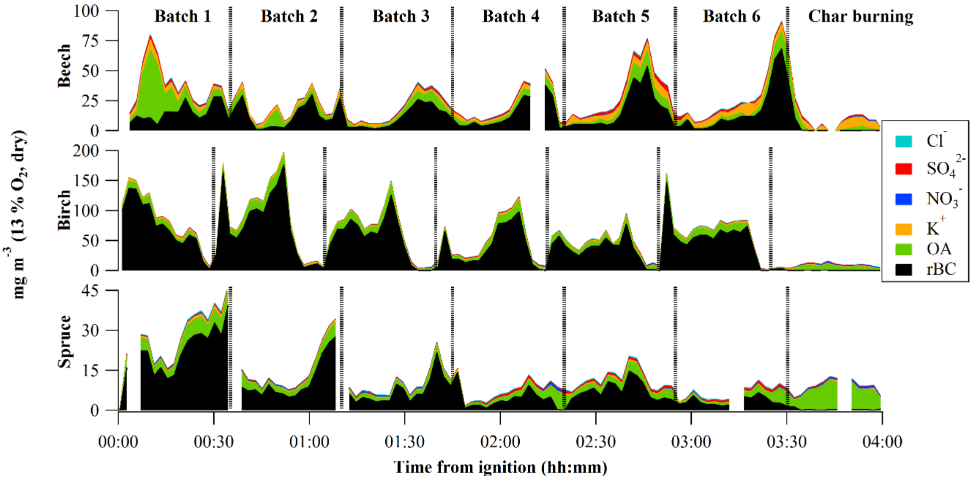

Fig. 5: Time-resolved chemical composition of particle emissions measured by HR-SP-AMS (**Paper II**).

5.3.2.2 Refractory black carbon

The formation of rBC takes place only when flame is visible (including ignition and stable combustion). Notable differences were observed in rBC formation, however, between the wood species. Birch combustion produced the highest average rBC emissions (Fig. 5). The time-resolved rBC emissions of birch showed two major periods of black carbon emission—at the ignition of a new batch and during the most intense combustion phase. In beech combustion, no such peak was observed at the beginning of a batch. Spruce combustion produced the lowest average rBC emissions. Most of the rBC from spruce was formed during the first two batches. For birch, the batch-to-batch variation of rBC was small throughout the experiment. In contrast, the concentration of rBC clearly increased for beech and decreased for spruce during combustion.

Unlike in previous research (Nuutinen, 2016), a correlation was observed between the emission of rBC and certain PAH compounds as measured by AMS (fluoranthene/pyrene). The strength of this correlation was dependent on the type of fuel. One explanatory factor for these PAHs and rBC being observed together is that PAHs are known precursors of soot (Kennedy, 1997). Another factor is that gaseous PAHs may be adsorbed onto the surface of soot, while remaining in the gas phase in the absence of soot.

5.3.2.3 Inorganics

Time-resolved information for major inorganic compounds were obtained from the SP-AMS measurements. In addition to K and Zn (Fig. 5 and Fig. 7, respectively), time-resolved emissions of chlorides, sulphates and nitrates were acquired (Fig. 6). The concentration of sulphates was notably highest for beech, which also had the highest fuel S content. Because of the available sulphates, the formation of nitrates was minor (formation of K_2SO_4 is thermodynamically favoured over KNO_3 (Sippula *et al.*, 2007). The case was different for birch and spruce as they contained less sulphur. The high availability of potassium in relation to sulphates and chlorides, especially during the char-burning phase, favoured the formation of potassium carbonates and nitrates. The release of K and Zn are discussed in Section 5.4.

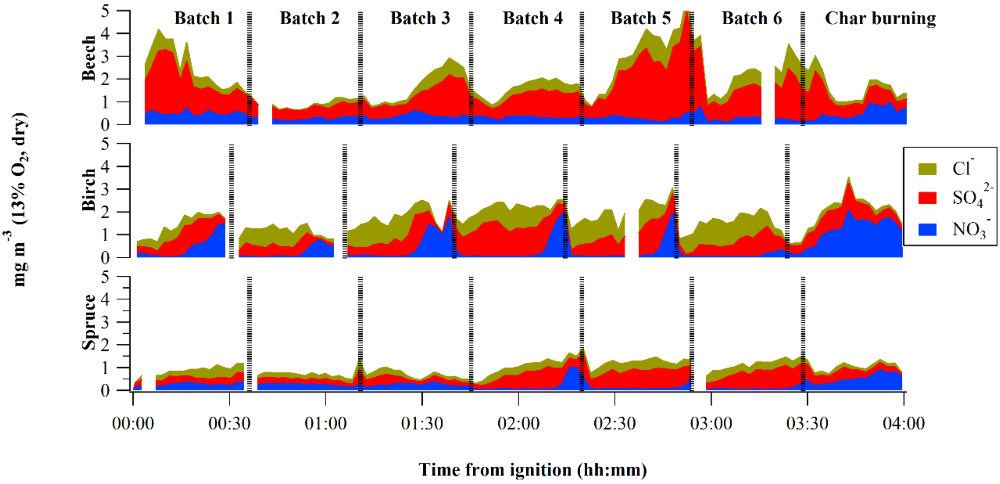

Fig. 6: Time-resolved concentrations of chloride, sulphate and nitrate from batch combustion experiments measured by HR-SP-AMS (**Paper II**).

5.4 Release of ash-forming elements and ash mass balances

The release of Zn and K was studied during continuous combustion using filter samples, and during batch combustion using both filters and AMS. In addition, Pb and Cu were investigated during the continuous combustion of wood and agricultural fuels using filter and bottom ash samples. The highest Zn emission was observed for reed canary grass co-combustion (averaging 787 µg MJ^{-1}). In batch combustion, birch produced the highest Zn emission (averaging 482 µg MJ^{-1}), which was comparable to emission during the continuous, non-optimal combustion of wood chips. In comparison, the smallest average Zn emission was produced by batch combustion of beech logs (averaging 35 µg MJ^{-1}). The release of Zn is known to be highly dependent not only on the fuel Zn concentration, but also on the fuel bed temperature (van Lith *et al.*, 2008). The low Zn emission from beech was attributed to its low Zn concentration. Low fuel Zn and low Zn emissions from beech in comparison to spruce have also been measured in previous studies (Orasche *et al.*, 2012; van Lith *et al.*, 2008).

The time-resolved emission of Zn during beech combustion did not show any distinct pattern, but was rather constant. For birch, Zn release was highest upon ignition of a new batch and during the most intense phase of combustion (Fig. 7). The initial peak was likely a product of the bark, which is known to have potentially high Zn concentrations compared to the stem wood. The second Zn peak (appearing at the end of each batch) probably resulted from the increasing fuel bed temperature combined with a reducing atmosphere which favours the release of zinc as Zn-vapour (Senior and Flagan, 1982). The Zn release from spruce combustion was lower compared to birch, and the release was highest during the char-burning phase.

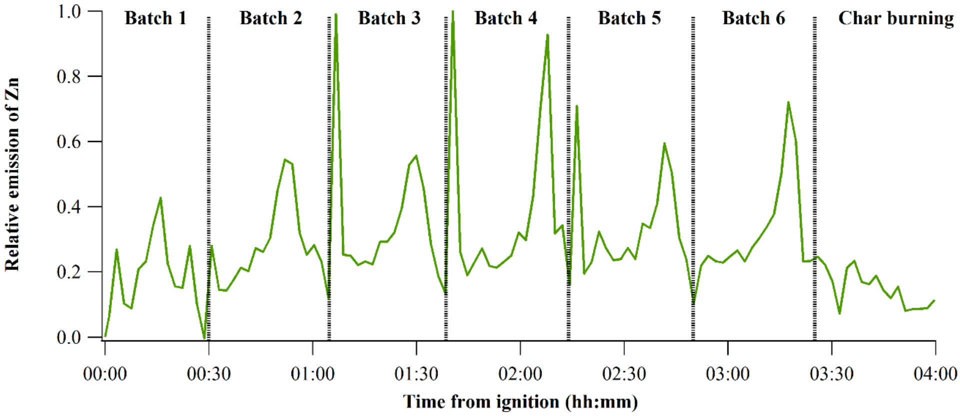

Fig. 7: Time-resolved release of zinc from birch combustion measured by HR-SP-AMS (**Paper II**).

In addition to Zn also Pb and Cu were present in notable quantities; Pb resulted mainly from the non-optimised combustion of wood chips and Cu mainly occurred during the co-combustion of wood and straw. In fact, limits for particle emissions from the incineration and co-incineration of waste (EC 2000/76) were exceeded in the non-optimal combustion of wood chips, where the concentration of Pb was particularly increased. Based on these results, the release of Pb seems to be sensitive to conditions in the fuel bed (**Paper I**: Fig. 3). The poor combustion scenario (Wood 4) in **Paper I** resulted in considerably increased Pb emission compared to more optimised combustion scenarios (Wood 1 – 3). The high Cu emission from wood and straw combustion was likely connected to the high Cl content of straw (**Paper I**: Table 2), which may lead to the formation of copper chloride ($CuCl_2$). This will enhance the release of Cu to the gas phase, later condensing onto the particles (Lind *et al.*, 2007).

Particle mass emission from batch combustion was dominated by EC and OC, and the share of inorganics was only 10 % at the most. The proportion of inorganic emissions, especially K, became higher, however, during the burnout phase. The release of K during the char oxidation phase is well established (van Lith *et al.*, 2008; Wornat *et al.*, 1995). The highest average particulate K emission was produced by the co-combustion of wood and straw. High K emission from straw combustion results from its high fuel K content in addition to a high Cl content, which further enhances the release of K as KCl.

Generally, batch combustion produced lower average emissions of inorganics compared to continuous combustion of wood chips or pellets. The maximum K emission of birch during the char burnout phase was similar to the average emission from the continuous combustion of wood.

For fuels with high a silicate/alkali ratio, alkalis are likely bound in the bottom ash as silicates more effectively. For all the fuels studied here, the Si/K ratio was by far the largest for the wood chip and reed canary grass mixture. The high particle formation during wood-straw combustion was mainly affected by the high concentration of K in the straw. K was also the main responsible of the high ash content of straw compared to reed canary grass.

The elemental analyses of bottom ash samples were performed for the continuous combustion of wood chips and blended agricultural fuels. All the samples were found to be eligible for use as either field or forest fertilisers (Ministry of Agriculture and Forestry of Finland, 2011). Thus, the recycling of bottom ash would not be a problem.

6 Review of papers and the author’s contribution

Paper I investigates the effect of small-scale co-combustion of wood and selected agricultural fuels on emissions and ash properties. Additionally, the effect of combustion air-staging on emissions was studied. The air-staging experiments, data analysis, interpretation and manuscript writing were carried out by the author under the supervision of Doc. O. Sippula and Prof. J. Jokiniemi.

Paper II presents highly time-resolved emissions data from small-scale batch combustion of three different wood species in a masonry heater. The data analysis and the manuscript writing were mainly carried out by the author. Additionally, the author operated the combustion device and contributed to the implementation of the experimental setup under the supervision of Doc. J. Tissari, Doc. O. Sippula and Prof. J. Jokiniemi. The study was carried out in cooperation with the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE).

Paper III investigates the temporal variation of organic emissions from batch-wise combustion of three European wood species combusted in a modern masonry heater. The study utilises Single Photon Ionisation Mass Spectrometry for determining the real-time emissions of volatile, intermediate-volatile and semivolatile organic compounds. The author was responsible for the operation of the combustion appliance and, partly, for the data analysis. Additionally, the author participated in the writing of the manuscript. The study was carried out in cooperation with the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) under the supervision of Prof. J. Jokiniemi and Prof. R. Zimmermann.

Paper IV investigates the emission factors of carbonyls from the batch combustion of three different wood species and the continuous combustion of softwood pellets. The carbonyl sampling was done with 2,4-dinitrophenylhydrazine cartridges and was analysed using Selective Ion Monitoring Gas Chromatography-Mass Spectrometry. The author was responsible for operating the combustion device and contributed to the data analysis and manuscript writing. The study was carried out in cooperation with the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) under the supervision of Prof. J. Jokiniemi and Prof. R. Zimmermann.

7 Conclusions

In this thesis, the physicochemical properties of emissions from various small-scale combustion appliances burning selected biomass fuels were determined. The effects of biomass raw material and combustion conditions on particulate and gaseous emissions were characterised in both batch and continuously operated combustion systems. Time dependency of emissions (both particulate and gaseous components) were comprehensively characterised from the batch combustion of wood logs and the continuous combustion of wood chips, blended agricultural fuels and softwood pellets. This area of research is important since wood is a common source of heat in detached houses, and utilisation of these fuels may increase due to current EU climate policy aiming to increase the share of renewables in final energy consumption.

The combustion air distribution in continuous combustion of wood chips affected the emission of fine particles and the emissions of incomplete combustion. Increasing the proportion of secondary air decreased the emissions of EC, OC, and CO. However, no major influence was observed on the release of ash compounds, except for certain trace metals, most notably Pb and Zn. For these elements, the release mechanism is probably governed by the prevailing conditions at the fuel bed (in this context, mainly the bed temperature and oxidising/reducing atmosphere).

The blending of reed canary grass with wood chips increased PM_1 mass emissions by about 40 % compared to pure wood chip combustion; however, the emission level remained reasonably low. The difference in mass emissions was mostly due to the slightly increased formation of KCl. Blending wood chips with straw increased PM_1 emissions considerably—by more than 13 times. The high concentrations of K and Cl in barley straw had a substantial effect on particle formation; particles from straw combustion were mainly composed of KCl and their crystalline structure deviated notably from the typical amorphous particles generated from wood combustion. These features of straw co-combustion indicate a high potential for causing operational problems through fouling of the heat exchanger surfaces, induced by deposition of ash with a high share of alkali chlorides. Another potential issue in the thermal utilisation of straw is the high fuel ash concentration and its low melting temperature resulting from the ash composition. The low melting temperature of ash often leads to slag formation and, therefore, a solid grate combustion system is not applicable for fuels of such quality. Finally, from an environmental viewpoint, high PM emissions from co-combustion of straw and wood chips would require an efficient flue gas cleaning system.

The utilisation of ashes is often a concern, especially for large combustion plants. In this study, addition of agricultural fuels was not found to significantly increase the amounts of harmful metals in the bottom ash fraction. As a result, the ash met Finnish national requirements for forest and field fertilisers. Therefore, the disposal of bottom ash from the small-scale co-combustion of wood and agricultural fuels would not likely pose a problem.

In the batch-wise combustion, wood species was observed to have an effect not only on the emission factors but also on the temporal variation of emissions. Common to all wood species was a high concentration of organic emissions during the ignition phase. During the ignition phase, temperatures are typically too low for efficient secondary combustion. The firebox temperature is also crucial considering the oxidation of elemental carbon emissions. Both OC and EC emissions decreased as the burning rate increased. During the char-burning phase, OC emissions decreased significantly and no EC formation was detected at all. The time-resolved emissions of rBC also indicated that formation only occurred during the flaming phase.

Differences between wood species were observed in the batch combustion with respect to particle mass emissions. This depended on the prevailing conditions in the firebox, which are partly determined by the properties of fuel. Based on these results, the efficient utilisation of secondary combustion air seems to have a decreasing effect on particle mass emission. The lowest mass emissions during stable burning were measured with the highest fuel bed height, which provided the smallest distance between the fuel bed and the secondary combustion air inlet, thereby leading to efficient mixing of combustion products and air (verified by low lambda values).

This study indicates that batch combustion produces significantly higher emissions of organics (e.g. carbonyls) compared to continuous pellet combustion; however, compared to previous studies over the last 15 years using open fireplaces and wood stoves, both appliances studied here had lower carbonyl emissions.

Zn-containing combustion-derived particles have been identified as inducing toxicological responses in lung cell lines. Zn is a common element in most solid biofuels. The release of Zn was found to be not only reliant on the fuel Zn content, but also highly time-dependent. With birch bark, a high share of Zn was released during each batch ignition phase. This can be explained by the fact that birch bark contains high concentrations of Zn and, for birch in particular, the ignition of bark is rapid. The release of Zn during stable combustion and char burning is governed by temperature and the prevailing conditions (i.e. whether oxidising or reducing).

Assessing the time-resolved emissions of the batch combustion process is an important step in identifying problematic combustion phases that produce elevated emissions, and for developing low-emission combustion devices. The batch combustion process is a series of complex events, some of which are overlapping and some consecutive. In this study, the ignition of the first batch was always performed from a ‘cold start’, which creates completely different combustion conditions compared to sequential batches, where the combustion chamber temperature is high from the outset. Furthermore, each batch has three fundamental combustion phases—ignition, stable combustion, and char burnout—and each of these phases produces characteristic emissions. The optimisation of the combustion process, considering all combustion phases and conditions, is not straightforward, especially because batch combustion devices are usually relatively simple appliances without automation. In small-scale combustion, primary measures for emission reduction should be utilised thoroughly before applying secondary methods, which often have an increased need for maintenance and involve higher costs in both acquisition and operation.

As a general conclusion, the type of biomass fuel used in small-scale combustion has an impact not only on the mass of fine particulate and gaseous emissions, but also on the chemical composition of PM_1. In this study, the batch combustion of spruce had clearly the lowest mass emission of fine particulate matter. This result may not apply for all combustion devices, but it shows that differences in emissions between wood species exists. The effect of fuel elemental composition on PM emissions was especially notable in the continuous combustion of wood and agricultural fuels. The temporal variation of the batch combustion emissions also revealed differences between wood species—mostly in the formation of black carbon and organic emissions. Slow ignition leads to a longer cold period in the combustion chamber and inefficient oxidation of devolatilisation products (organic compounds) results; fast ignition from the top of the batch is the most beneficial approach considering the associated reduction in emissions. This can be confirmed also by earlier studies.

Currently, emissions from different wood species are not taken into account in the compilation of emission inventories. Based on this research, such emissions are clearly variable, but challenging to estimate due to large variety of combustion appliances. A large variety in combustion appliances leads to large variety in combustion emissions. This likely increases the margin of error for emission inventories.

References

Adam T, Zimmermann R, (2007) Determination of single photon ionization cross sections for quantitative analysis of complex organic mixtures. *Analytical and Bioanalytical Chemistry* **389**(6): 1941-1951.

Ahtoniemi P, Tainio M, Tuomisto JT *et al.*, (2010) Health Risks from Nearby Sources of Fine Particulate Matter: Domestic Wood Combustion and Road Traffic (PILTTI) **3/2010**.

Alakangas E, Hurskainen M, Laatikainen-Luntama J, Korhonen J, (2016) Properties of indigenous fuels in Finland **272**.

Alén R, Kotilainen R, Zaman A, (2002) Thermochemical behavior of Norway spruce (Picea abies) at 180–225 °C. *Wood Science and Technology* **36**(2): 163-171.

Asbach C, Fissan H, Stahlmecke B, Kuhlbusch TAJ, Pui DYH, (2009) Conceptual limitations and extensions of lung-deposited Nanoparticle Surface Area Monitor (NSAM). *Journal of Nanoparticle Research* **11**(1): 101-109.

Atkinson R, (2000) Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment* **34**(12): 2063-2101.

Bankiewicz D, Enestam S, Yrjas P, Hupa M, (2013) Experimental studies of Zn and Pb induced high temperature corrosion of two commercial boiler steels. *Fuel Processing Technology* **105**(0): 89-97.

Baxter LL, Miles TR, Miles Jr. TR *et al.*, (1998) The behavior of inorganic material in biomass-fired power boilers: Field and laboratory experiences. *Fuel Processing Technology* **54**(1-3): 47.

Becidan M, Todorovic D, Skreiberg Ø *et al.*, (2012) Ash related behaviour in staged and non-staged combustion of biomass fuels and fuel mixtures. *Biomass and Bioenergy* **41**: 86-93.

Cai H-, Güell AJ, Chatzakis IN *et al.*, (1996) Combustion reactivity and morphological change in coal chars: Effect of pyrolysis temperature, heating rate and pressure. *Fuel* **75**(1): 15-24.

Carnö J, Berg M, Järås S, (1996) Catalytic abatement of emissions from small-scale combustion of wood: A comparison of the catalytic effect in model and real flue gases. *Fuel* **75**(8): 959-965.

Carvalho L, Wopienka E, Pointner C *et al.*, (2013) Performance of a pellet boiler fired with agricultural fuels. *Applied Energy* **104**: 286.

Cerqueira M, Gomes L, Tarelho L, Pio C, (2013) Formaldehyde and acetaldehyde emissions from residential wood combustion in Portugal. *Atmospheric Environment* **72**: 171-176.

Colonna P, Berloco N, Ranieri V, Shuler ST, (2012) Application of Bottom Ash for Pavement Binder Course. *Procedia - Social and Behavioral Sciences* **53**: 961-971.

Czech H, Pieber SM, Tiitta P *et al.*, (2017) Time-resolved analysis of primary volatile emissions and secondary aerosol formation potential from a small-scale pellet boiler. *Atmospheric Environment* **158**: 236-245.

Diab J, Streibel T, Cavalli F *et al.*, (2015) Hyphenation of a EC / OC thermalâ€“optical carbon analyzer to photo-ionization time-of-flight mass spectrometry: an off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter. *Atmospheric Measurement Techniques* **8**(8): 3337-3353.

Díaz-Ramírez M, Sebastián F, Royo J, Rezeau A, (2014) Influencing factors on NOX emission level during grate conversion of three pelletized energy crops. *Applied Energy* **115**(0): 360-373.

Elsasser M, Busch C, Orasche J *et al.*, (2013) Dynamic Changes of the Aerosol Composition and Concentration during Different Burning Phases of Wood Combustion. *Energy Fuels* **27**(8): 4959-4968.

Eriksson AC, Nordin EZ, Nyström R *et al.*, (2014) Particulate PAH Emissions from Residential Biomass Combustion: Time-Resolved Analysis with Aerosol Mass Spectrometry. *Environmental science & technology* **48**(12): 7143-7150.

Eskilsson D, Rönnbäck M, Samuelsson J, Tullin C, (2004) Optimisation of efficiency and emissions in pellet burners. *Biomass and Bioenergy* **27**(6): 541-546.

EU 2015/1189, Commission Regulation (EU) 2015/1189 of 28 April 2015 implementing Directive 2009/125/EC of the European Parliament and of the Council with regard to ecodesign requirements for solid fuel boilers (Text with EEA relevance).

EU 2000/76/EC, Directive 2000/76/EC of the European parliament and of the council of 4 December 2000 on the incineration of waste. Off J Eur Communities: L332/91. December 28 2000.

EUCO 169/14, European Council Conclusions, 24 October 2014, EUCO 169/14.

Evtyugina M, Alves C, Calvo A *et al.*, (2014) VOC emissions from residential combustion of Southern and mid-European woods. *Atmospheric Environment* **83**: 90-98.

Fagerström J, Näzelius I, Gilbe C *et al.*, (2014) Influence of Peat Ash Composition on Particle Emissions and Slag Formation in Biomass Grate Co-combustion. *Energy Fuels* **28**(5): 3403-3411.

Frey AK, Tissari J, Saarnio KM *et al.*, (2009) Chemical composition and mass size distribution of fine particulate matter emitted by a small masonry heater. *Boreal Environment Research* **14**: 255-271.

Gilbe C, Öhman M, Lindström E *et al.*, (2008) Slagging characteristics during residential combustion of biomass pellets. *Energy and Fuels* **22**(5): 3536-3543.

Grigonyte J, Nuutinen I, Koponen T *et al.*, (2014) Evaluation of a Heat Exchanger Designed for Efficient Fine Particle Precipitation in Small-Scale Wood Combustion. *Energy Fuels* **28**(9): 6058-6065.

Gröhn A, Suonmaa V, Auvinen A, Lehtinen KEJ, Jokiniemi J, (2009) Reduction of Fine Particle Emissions from Wood Combustion with Optimized Condensing Heat Exchangers. *Environmental science & technology* **43**(16): 6269-6274.

Grønli MG, Várhegyi G, Di Blasi C, (2002) Thermogravimetric Analysis and Devolatilization Kinetics of Wood. *Industrial & Engineering Chemistry Research* **41**(17): 4201-4208.

Hallquist M, Wenger JC, Baltensperger U *et al.*, (2009) The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics* **9**(14): 5155-5236.

Hedberg E, Kristensson A, Ohlsson M *et al.*, (2002) Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmospheric Environment* **36**(30): 4823-4837.

Heringa MF, DeCarlo PF, Chirico R *et al.*, (2012) Time-Resolved Characterization of Primary Emissions from Residential Wood Combustion Appliances. *Environmental science & technology* **46**(20): 11418-11425.

Hinds W,C., (1999) Aerosol technology: properties, behavior, and measurement of airborne particles, 2nd edn. New York: John Wiley & Sons, Inc.

Houshfar E, Løvås T, Skreiberg Ø, (2012) Experimental Investigation on NOx Reduction by Primary Measures in Biomass Combustion: Straw, Peat, Sewage Sludge, Forest Residues and Wood Pellets. *Energies* **5**(2): 270-290.

Hukkanen A, Kaivosoja T, Sippula O *et al.*, (2012) Reduction of gaseous and particulate emissions from small-scale wood combustion with a catalytic combustor. *Atmospheric Environment* **50**: 16-23.

Järup L, (2003) Hazards of heavy metal contamination. *British medical bulletin* **68**(1): 167-182.

Johansson LS, Leckner B, Gustavsson L *et al.*, (2004) Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. *Atmospheric Environment* **38**(25): 4183-4195.

Jokiniemi JK, Lazaridis M, Lehtinen KEJ, Kauppinen EI, (1994) Numerical simulation of vapour-aerosol dynamics in combustion processes. *Journal of Aerosol Science* **25**(3): 429-446.

Jordan TB, Seen AJ, (2005) Effect of Airflow Setting on the Organic Composition of Woodheater Emissions. *Environmental science & technology* **39**(10): 3601-3610.

Kaivosoja T, Jalava PI, Lamberg H *et al.*, (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. *Atmos.Environ.* **77**: 193-201.

Kennedy IM, (1997) Models of soot formation and oxidation. *Progress in Energy and Combustion Science* **23**(2): 95-132.

Keskinen J, Pietarinen K, Lehtimäki M, (1992) Electrical low pressure impactor. *Journal of Aerosol Science* **23**(4): 353-360.

Khan AA, de Jong W, Jansens PJ, Spliethoff H, (2009) Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Processing Technology* **90**(1): 21-50.

Kleinhans U, Halama S, Spliethoff H, (2017) The role of gasification reactions during pulverized solid fuel combustion: A detailed char combustion model based on measurements of char structure and kinetics for coal and pre-treated biomass. *Combustion and Flame* **184**: 117-135.

Knudsen JN, Jensen PA, Dam-Johansen K, (2004) Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy and Fuels* **18**(5): 1385.

Lamberg H, Nuutinen K, Tissari J *et al.*, (2011a) Physicochemical characterization of fine particles from small-scale wood combustion. *Atmos.Environ.* **45**(40): 7635-7643.

Lamberg H, Sippula O, Tissari J, Jokiniemi J, (2011b) Effects of air staging and load on fine-particle and gaseous emissions from a small-scale pellet boiler. *Energy and Fuels* **25**(11): 4952-4960.

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 and Fuels* **27**(11): 7044.

Leskinen J, Tissari J, Uski O *et al.*, (2014) Fine particle emissions in three different combustion conditions of a wood chip-fired appliance – Particulate physico-chemical properties and induced cell death. *Atmospheric Environment* **86**: 129-139.

Lind T, Hokkinen J, Jokiniemi JK, (2007) Fine particle and trace element emissions from waste combustion - Comparison of fluidized bed and grate firing. *Fuel Processing Technology* **88**(7): 737.

Lind T, Kauppinen EI, Hokkinen J *et al.*, (2006) Effect of chlorine and sulfur on fine particle formation in pilot-scale CFBC of biomass. *Energy & Fuels* **20**(1): 61-68.

Lipsky EM, Robinson AL, (2006) Effects of Dilution on Fine Particle Mass and Partitioning of Semivolatile Organics in Diesel Exhaust and Wood Smoke. *Environmental science & technology* **40**(1): 155-162.

Lyyränen J, Jokiniemi J, Kauppinen EI, Backman U, Vesala H, (2004) Comparison of Different Dilution Methods for Measuring Diesel Particle Emissions. *Aerosol Science and Technology* **38**(1): 12-23.

McMurry PH, (2000) The History of Condensation Nucleus Counters. *Aerosol Science and Technology* **33**(4): 297-322.

Ministry of Agriculture and Forestry. Decree on the fertilizer products 24/11 (1784/14/2011). September 13, 2011 [in Finnish].

Mühlberger F, Streibel T, Wieser J, Ulrich A, Zimmermann R, (2005) Single Photon Ionization Time-of-Flight Mass Spectrometry with a Pulsed Electron Beam Pumped Excimer VUV Lamp for On-Line Gas Analysis: Setup and First Results on Cigarette Smoke and Human Breath. *Analytical Chemistry* **77**(22): 7408-7414.

NIOSH Elemental Carbon (Diesel Particulate) Method 5040. In: NIOSH Manual of Analytical Methods (NMAM). Atlanta, GA: The National Institute for Occupational Safety and Health; 1999.

Nowakowska M, Herbinet O, Dufour A, Glaude P, (2014) Detailed kinetic study of anisole pyrolysis and oxidation to understand tar formation during biomass combustion and gasification. *Combustion and Flame* **161**(6): 1474-1488.

Nussbaumer T, (2003) Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction. *Energy and Fuels* **17**(6): 1510-1521.

Nuutinen K, (2016) Polycyclic aromatic hydrocarbon emissions from residential wood combustion. Report series in aerosol science (184). [PhD Thesis]. University of Eastern Finland. Kuopio, Finland; 2016.

Nuutinen K, Jokiniemi J, Sippula O *et al.*, (2014) Effect of air staging on fine particle, dust and gaseous emissions from masonry heaters. *Biomass and Bioenergy* **67**: 167-178.

Nyström R, Lindgren R, Avagyan R *et al.*, (2017) Influence of Wood Species and Burning Conditions on Particle Emission Characteristics in a Residential Wood Stove. *Energy & Fuels* **31**(5): 5514-5524.

Oasmaa A, Czernik S, (1999) Fuel Oil Quality of Biomass Pyrolysis OilsState of the Art for the End Users. *Energy Fuels* **13**(4): 914-921.

Obernberger I, Mandl C, (2011) Survey on the present state of particle precipitation devices for residential biomass combustion with a nominal capacity up to 50 kW in IEA Bioenergy Task32 member countries.

Obernberger I, (1998) Decentralized biomass combustion: state of the art and future development. *Biomass and Bioenergy* **14**(1): 33-56.

Obernberger I, Biedermann F, Widmann W, Riedl R, (1997) Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass and Bioenergy* **12**(3): 211-224.

Obernberger I, Brunner T, Bärnthaler G, (2006) Chemical properties of solid biofuels—significance and impact. *Biomass and Bioenergy* **30**(11): 973-982.

Öhman M, Boman C, Hedman H, Nordin A, Boström D, (2004) Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass and Bioenergy* **27**(6): 585-596.

Onasch TB, Trimborn A, Fortner EC *et al.*, (2012) Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application. *Aerosol Science and Technology* **46**(7): 804-817.

Orasche J, Seidel T, Hartmann H *et al.*, (2012) Comparison of Emissions from Wood Combustion. Part 1: Emission Factors and Characteristics from Different Small-Scale Residential Heating Appliances Considering Particulate Matter and Polycyclic Aromatic Hydrocarbon (PAH)-Related Toxicological Potential of Particle-Bound Organic Species. *Energy & Fuels* **26**(11): 6695-6704.

Patashnick H, Rupprecht EG, (1991) Continuous PM-10 Measurements Using the Tapered Element Oscillating Microbalance. *Journal of the Air & Waste Management Association* **41**(8): 1079-1083.

Pettersson E, Boman C, Westerholm R, Boström D, Nordin A, (2011) Stove Performance and Emission Characteristics in Residential Wood Log and Pellet Combustion, Part 2: Wood Stove. *Energy Fuels* **25**(1): 315-323.

Pope III CA, Dockery DW, (2006) Health effects of fine particulate air pollution: Lines that connect. *Journal of the Air and Waste Management Association* **56**(6): 709-742.

Reda AA, Czech H, Schnelle-Kreis J *et al.*, (2015) Analysis of Gas-Phase Carbonyl Compounds in Emissions from Modern Wood Combustion Appliances: Influence of Wood Type and Combustion Appliance. *Energy Fuels* **29**(6): 3897-3907.

Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S, (2011) A review on biomass as a fuel for boilers. *Renewable and Sustainable Energy Reviews* **15**(5): 2262-2289.

Salmenoja K, (2000) Field and laboratory studies on chlorine-induced superheater corrosion in boilers fired with biofuels.

Sarigiannis DA, Karakitsios SP, Gotti A, Liakos IL, Katsoyiannis A, (2011) Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk. *Environment International* **37**(4): 743-765.

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT, (2001) Measurement of Emissions from Air Pollution Sources. 3. C1-C29 Organic Compounds from Fireplace Combustion of Wood. *Environmental science & technology* **35**(9): 1716-1728.

Schwartz J, Neas LM, (2000) Fine particles are more strongly associated than coarse particles with acute respiratory health effects in schoolchildren. *Epidemiology* **11**(1): 6-10.

Senior CL, Flagan RC, (1982) Ash Vaporization and Condensation During Combustion of a Suspended Coal Particle. *Aerosol Science and Technology* **1**(4): 371-383.

SFS 5624. Air quality. Stationary source emissions. Determination of flue gas conditions. Finnish Standards Association; June 4, 1990.

Shin WG, Pui DYH, Fissan H, Neumann S, Trampe A, (2007) Calibration and numerical simulation of Nanoparticle Surface Area Monitor (TSI Model 3550 NSAM). *Journal of Nanoparticle Research* **9**(1): 61-69.

Sippula O, Hytonen K, Tissari J, Raunemaa T, Jokiniemi J, (2007) Effect of wood fuel on the emissions from a top-feed pellet stove. *Energy & Fuels* **21**(2): 1151-1160.

Sippula O, Lamberg H, Leskinen J, Tissari J, Jokiniemi J, (2017) Emissions and ash behavior in a 500kW pellet boiler operated with various blends of woody biomass and peat. *Fuel* **202**: 144-153.

Sippula O, Lind T, Jokiniemi J, (2008) Effects of chlorine and sulphur on particle formation in wood combustion performed in a laboratory scale reactor. *Fuel* **87**(12): 2425-2436.

Sommersacher P, Brunner T, Obernberger I, (2012) Fuel indexes: A novel method for the evaluation of relevant combustion properties of new biomass fuels. *Energy and Fuels* **26**(1): 380.

Statistics Finland, (2018). Official Statistics of Finland (OSF): Energy consumption in households [e-publication]. ISSN=2323-329X. Helsinki: Statistics Finland [referred: 26.11.2018]. Access method: http://www.stat.fi/til/asen/index_en.html

Tiitta P, Leskinen A, Hao L *et al.*, (2016) Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging. *Atmospheric Chemistry and Physics* **16**(20): 13251-13269.

Tilman D, Socolow R, Foley JA *et al.*, (2009) Beneficial Biofuels—The Food, Energy, and Environment Trilemma. *Science* **325**(5938): 270-271.

Tissari J, Hytönen K, Lyyränen J, Jokiniemi J, (2007) A novel field measurement method for determining fine particle and gas emissions from residential wood combustion. *Atmospheric Environment* **41**(37): 8330-8344.

Tissari J, Lyyränen J, Hytönen K *et al.*, (2008a) Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. *Atmospheric Environment* **42**(34): 7862-7873.

Tissari J, Sippula O, Kouki J, Vuorio K, Jokiniemi J, (2008b) Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. *Energy and Fuels* **22**(3): 2033.

Tissari J, Hytönen K, Sippula O, Jokiniemi J, (2009) The effects of operating conditions on emissions from masonry heaters and sauna stoves. *Biomass and Bioenergy* **33**(3): 513-520.

Torvela T, Tissari J, Sippula O *et al.*, (2014) Effect of wood combustion conditions on the morphology of freshly emitted fine particles. *Atmospheric Environment* **87**(0): 65-76.

Uski O, Jalava PI, Happo MS *et al.*, (2015) Effect of fuel zinc content on toxicological responses of particulate matter from pellet combustion in vitro. *Science of The Total Environment* **511**: 331-340.

van Eijk Rj, Obernberger I, Supancic K, (2012) Options for increased utilization of ash from biomass combustion and co-firing, IEA bioenergy task 32, Deliverable D4. Arnheim, March 5, 2012.

van Lith SC, Jensen PA, Frandsen FJ, Glarborg P, (2008) Release to the gas phase of inorganic elements during wood combustion. Part 2: influence of fuel composition. *Energy & Fuels* **22**(3): 1598-1609.

van Loo S, Koppejan J (Eds.), (2008) The Handbook of Biomass Combustion and Co-firing. London: Earthscan.

Vassilev SV, Baxter D, Andersen LK, Vassileva CG, (2010) An overview of the chemical composition of biomass. *Fuel* **89**(5): 913-933.

Vassilev SV, Baxter D, Vassileva CG, (2014) An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel* **117, Part A**(0): 152-183.

Vicente ED, Duarte MA, Calvo AI *et al.*, (2015) Emission of carbon monoxide, total hydrocarbons and particulate matter during wood combustion in a stove operating under distinct conditions. *Fuel Processing Technology* **131**(Supplement C): 182-192.

Wang G, Shen L, Sheng C, (2012) Characterization of Biomass Ashes from Power Plants Firing Agricultural Residues. *Energy & Fuels* **26**(1): 102-111.

Wang SC, Flagan RC, (1990) Scanning Electrical Mobility Spectrometer. *Aerosol Science and Technology* **13**(2): 230-240.

Wiinikka H, Gebart R, Boman C, Boström D, Öhman M, (2007) Influence of fuel ash composition on high temperature aerosol formation in fixed bed combustion of woody biomass pellets. *Fuel* **86**(1-2): 181-193.

Wornat MJ, Hurt RH, Yang NYC, Headley TJ, (1995) Structural and compositional transformations of biomass chars during combustion. *Combustion and Flame* **100**(1): 131-143.

Zaman A, Alén R, Kotilainen R, (2000) Thermal behavior of scots pine (Pinus Sylvestris) and silver birch (Betula Pendula) at 200-230 °C. *Wood and Fiber Science* **32**(2): 138-143.

APPENDIX I

Table 5: Ash fusion temperatures of pure fuels (oxidising conditions).

	Deformation temperature °C (DT)	**Spherical temperature °C (ST)**	**Hemispherical temperature °C (HT)**	**Fluid/Flow temperature °C (FT)**
Wood chips (co-combustion)	1450	>1450	>1450	>1450
Reed canary grass	1260	1290	1370	1400
Straw	970	1100	1110	1150