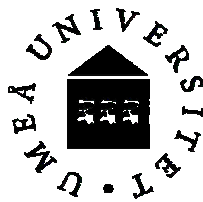


Particulate and gaseous emissions from residential biomass combustion

Christoffer Boman



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ABSTRACT

Biomass is considered to be a sustainable energy source with significant potentials for replacing electricity and fossil fuels, not at least in the residential sector. However, present wood combustion is a major source of ambient concentrations of hydrocarbons (e.g. VOC and PAH) and particulate matter (PM) and exposure to these pollutants have been associated with adverse health effects. Increased focus on combustion related particulate emissions has been seen concerning the formation, characteristics and implications to human health. Upgraded biomass fuels (e.g. pellets) provide possibilities of more controlled and optimized combustion with less emission of products of incomplete combustion (PIC's). For air quality and health impact assessments, regulatory standards and evaluations concerning residential biomass combustion, there is still a need for detailed emission characterization and quantification when using different fuels and combustion techniques.

This thesis summarizes the results from seven different papers. The overall objective was to carefully and systematically study the emissions from residential biomass combustion with respect to: i) experimental characterization and quantification, ii) influences of fuel, appliance and operational variables and iii) aspects of ash and trace element transformations and aerosol formation. Special concern in the work was on sampling, quantification and characterization of particulate emissions using different appliances, fuels and operating procedures.

An initial review of health effects showed epidemiological evidence of potential adverse effect from wood smoke exposure. A robust whole flow dilution sampling set-up for residential biomass appliances was then designed, constructed and evaluated, and subsequently used in the following emission studies. Extensive quantifications and characterizations of particulate and gases emissions were performed for residential wood and pellet appliances. Emission factor ranges for different stoves were determined with variations in fuel, appliance and operational properties. The emissions of PIC's as well as PM_{tot} from wood combustion were in general shown to be considerably higher compared to pellets combustion. PAH_{tot} emissions were determined in the range of 1300-220000 $\mu\text{g}/\text{MJ}$ for wood stoves and 2-300 $\mu\text{g}/\text{MJ}$ for pellet stoves with phenanthrene, fluoranthene and pyrene generally found as major PAH's. The PM emissions from present residential appliances was found to consist of significant but varying fractions of PIC's, with emissions in the range 35-350 mg/MJ for wood stoves compared to 15-45 mg/MJ for pellet stoves. Accordingly, the use of up-graded biomass fuels, combusted under continuous and controlled conditions give advantageous combustion conditions compared to traditional batch wise firing of wood logs. The importance of high temperature in well mixed isothermal conditions was further illustrated during pellets combustion to obtain complete combustion with almost a total depletion of PIC's. Fine (100-300 nm) particles dominated in all studied cases the PM with 80-95% as PM_1 . Beside varying fractions of carbonaceous material, the fine PM consisted of inorganic volatilized ash elements, mainly found as KCl, $K_3Na(SO_4)_2$ and K_2SO_4 with mass concentrations at 15-20 mg/MJ during complete combustion. The importance of the behavior of alkali elements for the ash transformation and fine particle formation processes was further shown, since the stability, distributions and compositions also directly control the degree of volatilization. In addition to the alkali metals, zinc was found as an important element in fine particles from residential biomass combustion. Finally, the behaviour of volatile trace elements, e.g. Zn and Cd, during pellets production and combustion were studied. A significant enrichment in the pellet fuel during the drying process was determined. The magnitude and importance of the enrichment was, however, relative small and some alternative measures for prevention were also suggested.

KEYWORDS: aerosols, air pollution, emissions, fuel pellets, residential biomass combustion, inorganic characterization, incomplete combustion, particulate matter, polycyclic aromatic hydrocarbons, trace elements

45 pages and 7 appended papers

Particulate and gaseous emissions from residential biomass combustion

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This thesis includes the following papers, in the text referred to by their Roman numerals I-VII:

- I **Adverse health effects from ambient air pollution in relation to residential wood combustion in modern society**

BC Boman, AB Forsberg, BG Järvholm
Scandinavian Journal of Work, Environment and Health 2003;29(4):251-260
- II **Evaluation of a constant volume sampling set-up for residential biomass fired appliances - influence of dilution conditions on particulate and PAH emissions**

C Boman, A Nordin, R Westerholm, E Pettersson
Submitted to Biomass and Bioenergy
- III **Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels**

C Boman, A Nordin, D Boström, M Öhman
Energy and Fuels 2004;18:338-348
- IV **Slagging tendencies of wood pellet ash during combustion in residential pellet burners**

M Öhman, C Boman, H Hedman, A Nordin, D Boström
Biomass and Bioenergy 2004;27(6):585-596
- V **Gaseous and particulate emissions from combustion in residential wood log and pellet stoves - experimental characterization and quantification**

C Boman, E Pettersson, A Nordin, R Westerholm, D Boström
Manuscript
- VI **Effects of temperature and residence time on emission characteristics during fixed-bed combustion of conifer stem-wood pellets**

C Boman, E Pettersson, F Lindmark, M Öhman, A Nordin, R Westerholm
Manuscript
- VII **Trace element enrichment and behavior in wood pellet production and combustion processes**

C Boman, M Öhman, A Nordin
Manuscript

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Behndig AF, Mudway IS, Brown JL, Stenfors N, Helleday R, Duggan ST, Wilson SJ, Boman C, Cassee FR, Frew AJ, Kelly FJ, Sandström T, Blomberg A. *Airway antioxidant and inflammatory responses to diesel exhaust exposure in healthy humans*. Submitted to European Respiratory Journal.

Technical reports

Boman C, Nordin A, Westerholm R, Öhman M, Boström D. *Emissions from small-scale combustion of biomass fuels - extensive quantification and characterization*. STEM Report, Feb 2005.

Öhman M, Boman C, Hedman H, Nordin A, Pettersson P, Lethikangas P, Boström D, Westerholm R. *Beläggnings-/slaggbildning och partikelutsläpp vid förbränning av olika pelletskvaliteter i pelletsbrännare (<20 kW)*. STEM Report, Oct 2000.

Nordin A, Pettersson E, Öhman M, Boman C. *Systematisk emissionsminimering – småskaliga anläggningar*. STEM Report 2000.

Conference proceedings

Boman C, Nordin A, Westerholm R, Boström D. *Characterization and quantification of PAH and particle emissions during combustion in residential wood log and pellet stoves*. NOSA - Nordic Society for Aerosol Research. Annual Symposium. Stockholm, Sweden. November 11-12, 2004.

Lundholm K, Boman C, Boström D, Nordin A. *Fate of Cu, Cr and As and particle characteristics during co-combustion of impregnated wood and peat - chemical equilibrium and experimental results*. NOSA - Nordic Society for Aerosol Research. Annual Symposium. Stockholm, Sweden. November 11-12, 2004.

Boman C, Nordin A, Westerholm R, Öhman M, Boström D. *Systematic characterization and quantification of gaseous and particulate emissions from present residential wood and pellet stoves and potentials for future technology*. 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection. Rome, Italy. May 10-14, 2004.

Boman C, Lindmark F, Nordin A, Westerholm R. *Effect of temperature and residence time on the emission characteristics from isothermal combustion of biomass pellets*. 8th International Congress on Toxic Combustion By-Products: Origin, Fate and Health Impacts. Umeå, Sweden. June 17-19, 2003.

Öhman M, Boman C, Hedman H, Nordin A, Boström D. *Slagging tendencies of wood pellet ash during combustion in residential pellet burners*. The First World Conference on Pellets. Stockholm, Sweden. September 2-4, 2002.

Boman C, Nordin A, D Boström, Öhman M, Pettersson E. *Characterization of inorganic particulate matter from domestic combustion of pelletized biomass fuels*. NOSA - Nordic Society for Aerosol Research. Annual Symposium. Lund, Sweden. November 8-9, 2001.

Boman C, Nordin A, D Boström, Öhman M, Pettersson E. *Characterization of inorganic particulate matter from domestic combustion of pelletized biomass fuels*. Nordic Seminar on Pollutants and Inorganic Chemistry in Combustion. Lyngby, Denmark. October 22-23, 2001.

Boman C, Nordin A, Boström D, Öhman M, Pettersson E. *Particle emission characteristics from small-scale (< 20 kW) biomass combustion with six different pelletized fuels*. 7th International Congress on Combustion By-Products: Origin, Fate and Health Effects. Durham, North Carolina, USA. June 4-6, 2001.

CONTRIBUTION OF THE AUTHOR OF THIS THESIS

Paper I

The author performed the literature searching work and wrote the paper. The planning of the work as well as evaluation and interpretation of the results were performed in close cooperation with the co-authors.

Paper II

The major part of the experimental work (i.e. combustion experiments) was performed by the author who also contributed substantially in the planning, designing and construction of the sampling set-up. The evaluation of the results and writing of the paper was also made by the author.

Paper III

The author contributed substantially in the planning and accomplishment of the combustion experimental work. He also performed the SEM/EDS, parts of the XRD analysis and the chemical equilibrium model calculations, as well as wrote the paper. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

Paper IV

In accordance with paper III, Boman contributed substantially in the planning and accomplishment of the combustion experimental work and also performed the chemical equilibrium model calculations. He was further involved in the evaluation of the results as well as in the final editing of the paper.

Paper V

Boman was main responsible for the planning and accomplishment of the experimental work. Most of the experimental work was, however, performed by personal at Energy Technology Center in Piteå. He also performed the major part of the evaluation of the results, performed most of the SEM/EDS analysis work and wrote the paper.

Paper VI

Planning of the work and construction of the experimental reactor was to a substantially share made by the author. Boman also supervised a Master student (F Lindmark) who performed most of the experimental work (i.e. combustion experiments). He also performed the major part of the evaluation of the results, performed the SEM/EDS analysis, parts of the XRD analysis and wrote the paper.

Paper VII

The author contributed substantially to the evaluation of the field sampling results, he performed the chemical equilibrium model calculations and wrote the paper. The overall evaluation and interpretation of both the experimental field sampling and theoretical modeling results were performed in close cooperation with the co-authors.

ABBREVIATIONS

CCC	Central Composite Circumscribed
CMD	Count Median Diameter
CO	Carbon Oxide
CO ₂	Carbon Dioxide
CPC	Condensation Particle Counter
CVS	Continuous Volume Sampling
DMA	Differential Mobility Analyzer
EDS	Energy-Dispersive Spectroscopy
ESEM	Environmental Scanning Electron Microscopy
FD	Factorial Design
FFD	Full Factorial Design
GC-FID	Gas Chromatography-Flame Ionization Detection
GC-MS	Gas Chromatography-Mass Spectrometry
HEPA	High Efficiency Particulate Air
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
IR	Infrared
LPI	Low Pressure Impactor
MMD	Mass Median Diameter
NDIR	Non-Dispersive Infrared
NMVOC	Non-Methane Volatile Organic Compounds
NO	Nitrogen Oxide
NO ₂	Nitrogen Dioxide
NO _x	Nitrogen Oxides (NO+NO ₂)
OGC	Organic Gaseous Carbon
PAH	Polycyclic Aromatic Hydrocarbons
PCA	Principal Component Analysis
PIC	Product of Incomplete Combustion
PLS	Projection to Latent Structures by means of Partial Least Square Analysis
PM	Particulate Matter
PM _{tot}	Total sampled PM
PM _{1/2.5/10}	PM with aerodynamic particle diameters <1/2.5/10 μm
PUF	Polyurethane Foam
RWC	Residential Wood Combustion
SED	Statistical Experimental Design
SEM	Scanning Electron Microscopy
SMPS	Scanning Mobility Particle Sizer
SO ₂	Sulfur Dioxide
THC	Total (gaseous) Hydrocarbons
TOC	Total Organic Compounds
VOC	Volatile Organic Compounds
XAFS	X-Ray Absorption Fine Structure
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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1 INTRODUCTION

1.1 Background

The energy systems in the developed part of the world will most probably face considerable changes during the near future mainly related to the finite resources of oil and the increased concerns about the potential impact on the global climate from fossil fuel combustion. An increasing interest for biomass as a renewable and CO₂-neutral energy source has therefore been seen during the last decades with significant potential as a sustainable alternative to fossil fuels and nuclear power [1, 2]. Utilization of biomass by combustion or other thermochemical conversion processes (i.e. gasification and pyrolysis) is presently used mainly for production of heat and power but also with increasing focus on liquid fuel production. Beside the issue of CO₂ and other "greenhouse" gases, combustion processes is unfortunately also a major source of a large number of many classical air pollutants of environmental health concern, e.g. SO₂, NO₂, hydrocarbons and particulate matter (PM). Today there is an increased focus on combustion related particulate air pollution and its implications both on global warming [3] and human health [4].

In the industrialized world and in colder climate, biomass is mainly used for producing heat, either in large and medium sized district heating systems or in residential wood log boilers, stoves and fireplaces. Residential wood combustion (RWC) is actually considered as one of the major emission sources of ambient air pollution and the potential adverse health effects of volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH) and PM are of special concern [5, 6, 7]. In a local urban perspective, extensive use of this kind of small-scale emission sources can severely deteriorate the air quality in residential areas, especially during wintertime and at specific meteorological conditions. To evaluate the present use and facilitate a potential increased future use of biomass as energy source in an environmentally acceptable way, it is therefore important to carefully study the influences of combustion technology and fuel characteristics on air quality and human health. New and upgraded biomass fuels have also become more common, especially in Europe and North America, of which wood fuel pellets are especially well suited for the residential market [8, 9]. This residential pellet market is, however, relatively new and significant potentials for development and improvements concerning issues related to fuel quality, combustion technology and regulatory standards therefore exists. In Sweden, extensive research activities concerning biomass combustion have been in progress for quite a while. Several recent national research programs have been financed by the Swedish Energy Agency where the programs "Small-Scale Combustion of Biomass" [10] and "Emissions and Air Quality" with the sub-program "Biofuel, Health and Environment" [11] are of special relevance here. All of the work within the present thesis has been performed within the framework of one or the other of these national research programs. Accordingly, the research presented in this thesis was performed in light of the ongoing ambitions to increase the utilization of biomass based energy together with the increasing concern about combustion related air pollution and potential adverse health effects in present and future energy systems.

1.2 Emission history and environmental health

Peoples concern over ambient air pollution has followed the development of societies over a long time and even in ancient Greece and the Roman Empire, adverse health effects of poor air quality were noticed [12]. During the antiquity, wood was used as fuel and not until the 13th century coal was introduced with London as the first city with extensive coal combustion. Severe air pollution problems were, however, observed in many cities in England and Scotland and in 1307, the use of coal was forbidden. The authorities attempt to control the domestic combustion of coal had, however, little effect [13]. The industrialism and colder climate during the 17th century lead to increased demand for coal as fuel and accordingly followed by even more urban air pollution problems. From that time, the "London smog" - a mixture of sulfurous gases (i.e. SO₂) and soot particles - became a well known threat to human health. The most severe smog episode is the one in London in 1952 when unfavourable metrological conditions embedded the city in acid smoke pollution. Previous estimates [14] of 4000 excess deaths as a result of the smog episode have later been reassessed to about 12000 excess deaths [15].

The air pollution catastrophe in 1952 can be considered as the start for a more serious attitude and preventive work regarding air pollution and environmental health issues. Beside the emissions of SO₂ and soot from residential coal heating, pollutants like nitric oxides (NO_x) and carbon monoxide (CO) from an increased traffic during the 20th century, have been of special concern. The potential for traffic related emissions to form secondary air pollutant via atmospheric reactions, generally called photochemical smog, was first observed in Los Angeles in the 1940s [12]. During the last 50 years, the focus has been on these "classical" air pollutants and during the 1970s and 80s, the environmental effects and control of acid rain forming pollutants (i.e. NO_x and SO₂) were of special importance.

After considerable measures were taken for reducing these emissions by replacing coal for domestic heating and emission control strategies for the industry and traffic sector the focus on residential wood combustion (RWC) as a potential air pollution source increased. During the 1990s, the considerable emissions of hydrocarbons (e.g. PAH) from RWC and their carcinogenic effects was considered important and especially in USA, some work on wood combustion emissions were performed. The interest for particulate air pollution and the potential adverse health effects following exposure have thereafter increased drastically. A vast number of epidemiological studies have been published since the beginning of the 1990s when unexpectedly large health effects of relatively low concentrations of particulate air pollution was presented in several studies in USA [16]. Although extensive evidence on the associations between ambient particulate pollution and respiratory and cardiovascular mortality and morbidity exists, the links to different particle properties or components have yet not been identified [17]. Urban air pollution, its sources and implications on the environment and human health, is for several reasons therefore of great concern with an increased focus [18, 19] on the formation, characteristics and toxicological effects of combustion related fine (<1 µm) and ultrafine (<0.1 µm) particulate emissions.

1.3 Biomass for energy in perspective

Ever since man learned how to control fire, the phenomenon of combustion has been an indispensable part of the development of humanity and its societies. Combustion of biomass is accordingly the oldest and still today the worldwide most spread out energy source used in a variety of applications for production of heat and power as well as for cooking. In the developing part of the world, the every-day life for a majority of the people is dependent on fuels like wood, animal dung and crop residues [20, 21]. In the mid 18th century, wood contributed to over 90% of the total energy consumption in the United States, but has since then decreased considerably, both in actual and relative terms mainly to the favour of fossil fuels [22]. Today, only a small fraction (~11%) of the total global energy consumption is based on biomass fuels or other combustible renewable materials and waste [23] (Figure 1a). During the last decades, increasing interests in renewable, sustainable and CO₂-neutral energy production have been seen in the western world among politicians, authorities and industry. The research, development and implementation activities for biomass utilization have increased remarkably [24]. In Sweden, the energy political goals include a phase out of nuclear power and a significant decrease in the use of fossil fuels within a relatively near future. The total energy supply in Sweden 2003 was 624 TWh_a [25] and is estimated to be approximately the same in the future. Contributions from solar, wind and other renewable energy sources are further estimated to be relatively minor during the same period of time. On the other hand, the potential for biomass fuels is considerable and official estimates have concluded that the present biomass supply (including peat, waste, forestry and agriculture based fuels) of about 103 TWh_a can be increased up to a maximum of 230 TWh_a [26, 27]. Within the residential sector 44 TWh_a was used for heating purposes in residential houses in Sweden in 2002, of which approximately 12 TWh_a comes from biomass, mainly wood log with minor parts (1-2 TWh_a) as wood pellets [22, 28] (Figure 1b).

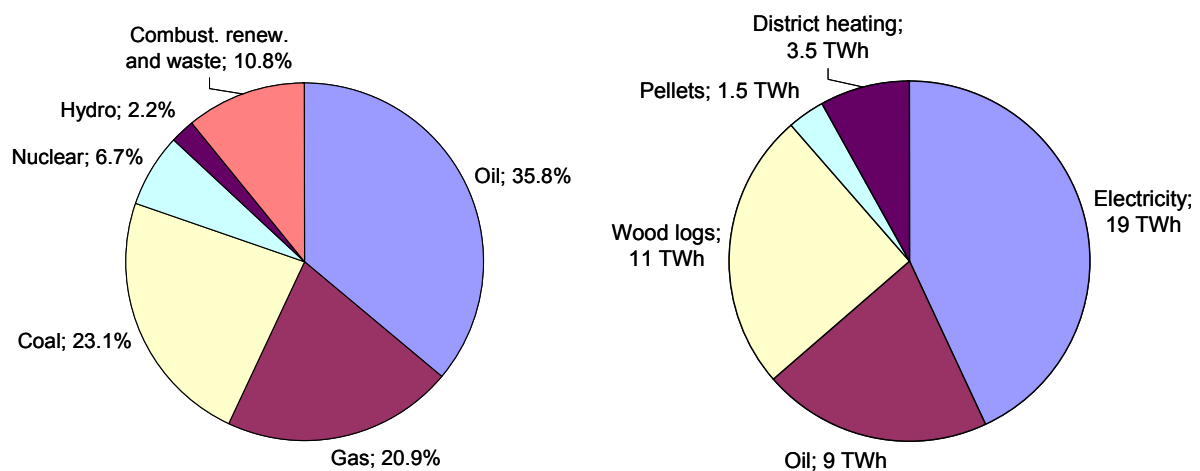


Figure 1. a) World total primary energy supply in 2002 (left) [23] and b) Use of energy for residential heating in Sweden in 2002 (right) [22, 28].

The potential for conversion from heating by oil, wood logs or electricity to fuel pellets is therefore considerable within the residential sector. Fuel pellets as well as briquettes are upgraded biomass fuels with several advantages during handling, storage and combustion compared to unprocessed wood fuels, e.g. wood chips, planar shavings and wood logs. The dried, densified and homogeneous fuel qualities provides possibilities to accomplish well controlled and optimized combustion conditions with high combustion efficiency and low emissions of products of incomplete combustion (PIC's). The development of systems for production and use of biomass fuel pellets have been extensive during the last decade mainly in Europe (e.g. Sweden, Austria and Germany) and North America [8, 9]. Since the beginning of the 1990s, the total use of pellets in Sweden has increased from only marginal to over 1 million tons annually (~5 TWh_a) of which approximately 25% presently goes to the residential sector [29]. Accordingly, the future potential for residential biomass combustion is on the use of up-graded wood fuels, e.g. pellets, combusted in well adapted and optimized appliances. In addition, the on-going use and development of new and improved wood log combustion technology is significant and will presumably enable a continued significant share of wood log combustion in different residential primary or secondary heating sources, i.e. boilers, stoves and fireplaces.

1.4 Combustion principles, by-products and aerosols

Combustion is an exothermic process where the combustible material (e.g. carbon and hydrogen) is oxidized to CO₂ and H₂O. Also elements like nitrogen and sulfur are more or less oxidized mainly to NO and SO₂. Chemically stored energy in the fuel is then converted to heat and radiation to be utilized in different ways. The basic conditions required for obtaining complete combustion, assuming air (i.e. oxygen) to be the oxidizing media, are well known and can be defined as;

- i) supply of air for complete oxidation*
- ii) sufficiently high temperature for chemical reaction kinetics*
- iii) sufficiently long residence time at high temperature (i.e. chemical reaction time)*
- iv) sufficient mixing (turbulence) of fuel components and air*

In almost all practical combustion situations, these conditions are not simultaneously and completely fulfilled and PIC's are formed as solid or gaseous by-products. PIC's are different kinds of carbonaceous material consisting of pyrolysis products (i.e. wood degradation products), VOC, PAH and soot particles. The number of different kinds of organic compounds that may be formed as a result of incomplete combustion conditions are considerable and besides pure hydrocarbons and oxygenated hydrocarbons, the potential formation of highly toxic chlorinated compounds like polychlorinated dibenzo dioxins (PCDD) and furans (PCDF) is also of special environmental health concern [30].

In solid (and liquid) fuels, a minor part of the fuel consists of incombustible ash forming matter and trace elements. Compared to coal, where the ash is dominated by mineral inclusions containing silicon (Si), aluminum (Al) and iron (Fe), biomass fuels are more rich in nutrient elements like calcium (Ca), potassium (K), sodium (Na) and phosphorus (P). This and other differences (e.g. higher oxygen to carbon ratio) makes the combustion properties and ash transformation processes significantly different for biomass fuels compared to coal [31]. The combustion process of a specific fuel particle proceeds in different distinct steps that schematically can be divided into drying, pyrolysis (devolatilization) and char combustion [32]. In a real application with continuous fuel feeding these sub-processes will occur simultaneously within the fuel bed. In batch wise combustion, however, a more distinct separation between the stages (volatilization and char combustion) is present which resembles the schematic illustration of the different main stages during combustion of a single biomass fuel particle in Figure 2. The figure attempts to briefly illustrate both the basic steps during thermal conversion of the fuel and the formation of different by-products including aerosols, of which some constitute the focus of the work in the present thesis.

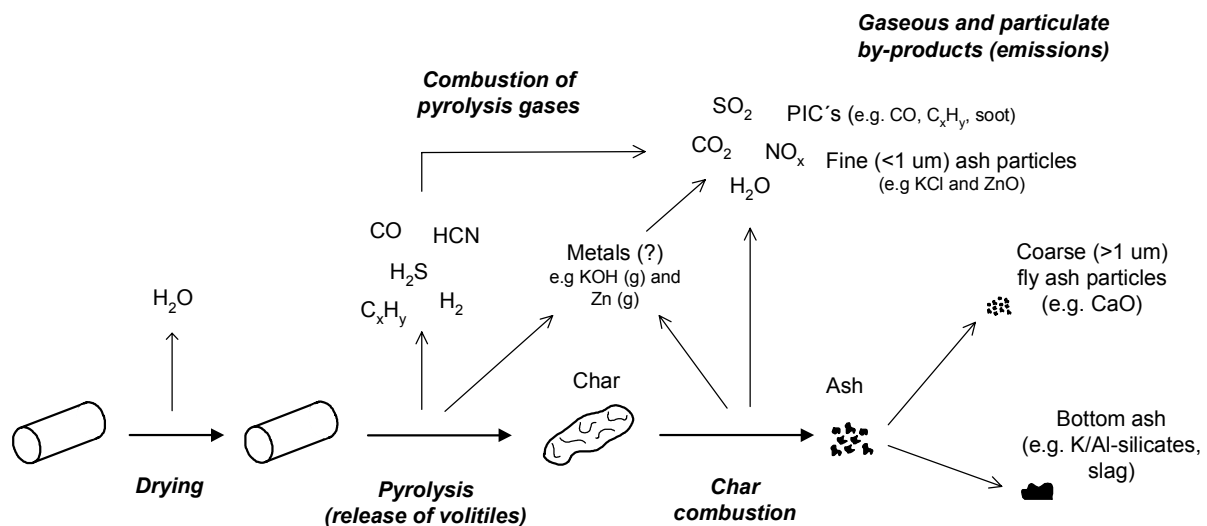


Figure 2. Schematic illustration of the different stages during combustion of a biomass fuel particle.

Aerosols are defined as solid or liquid particles suspended in a gas and ranges in particle size from 0.001 to over 100 μm . Due to the vast size range and complex chemical and physical processes controlling the formation and fate of aerosols of different kinds their properties and behavior can vary considerably [33]. Combustion related aerosols can generally be divided both in typical size fractions, i.e. coarse ($>1 \mu\text{m}$), fine ($<1 \mu\text{m}$) and ultrafine ($<0.1 \mu\text{m}$), but also based on origin, formation and chemical composition. During incomplete combustion, carbonaceous material in the form of un-oxidized hydrocarbons and soot particles is formed already in the flame region. At combustion temperatures, un-oxidized hydrocarbons exist in the gas phase until cooling of the flue gases and subsequent

condensation. Soot, however, are solid carbon structures in the size of a few nanometer, primarily formed in reducing atmospheres of flames [34]. Soot emissions from internal engine combustion (mainly diesel engines) have been of special concern and extensively studied with regard to formation, characteristics and control devices [35]. The formation mechanism of soot is very complex and a well adapted soot formation mechanism, via polycyclic aromatic cluster formation, particle inception, surface growth and coagulation (i.e. particle-particle collisions) was given by Bockhorn [36]. Residential wood combustion is also considered as a major emission source of PIC's, including soot particles, caused by air starving, temperature in-homogeneities and/or short residence times at sufficiently high temperatures. In larger appliances for solid fuel combustion, the combustion conditions can generally be better controlled and more complete.

During complete combustion of solid fuels, the particulate matter entirely consists of fractions of the incombustible ash forming matter in the fuel. The transformation and distribution of this inorganic matter to different ash fractions has been extensively elucidated and documented for coal combustion [38]. Detailed descriptions of the elucidated ash and aerosol forming processes during coal combustion have been described by several authors previously [39, 40, 41, 42]. Typically, coarse "fly ash" particles consist of mineral grains of refractory elements like silicon, aluminum and iron in the range of 1-50 μm , entrained from the fuel bed during combustion. The formation of fine combustion aerosols is generally initiated by the volatilization of ash forming elements within burning fuel particles with the subsequent processes of nucleation (homogeneous or heterogeneous), condensation and coagulation during cooling of the flue gases.

For biomass combustion, however, more scarce information concerning the behavior of ash forming elements during combustion was previously available [47] but have increased considerably during the last 5-10 years. In accordance with the general increased use of biomass instead of coal and other energy sources, the need for a better understanding of the specific biomass combustion related thermal conversion processes has been enhanced. The focus for the research has mainly been on the transformation of the relatively high concentrations of alkali metals, their fate and forms and aspects of ash related problems such as slagging, fouling, bed agglomeration and high temperature corrosion. Also the presence and behavior of biomass related trace elements, e.g. zinc and cadmium, have been of concern. The understanding of the processes governing the ash transformation and aerosol formation in biomass combustion systems have therefore continuously been refined and in Figure 3, a more detailed recently presented schematic illustration of the ash formation and aerosol processes during combustion of biomass is shown. Extensive research activities are today in progress in Europe and elsewhere concerning aerosols in biomass combustion; including formation, characterization, behaviour, emissions and health effects [48].

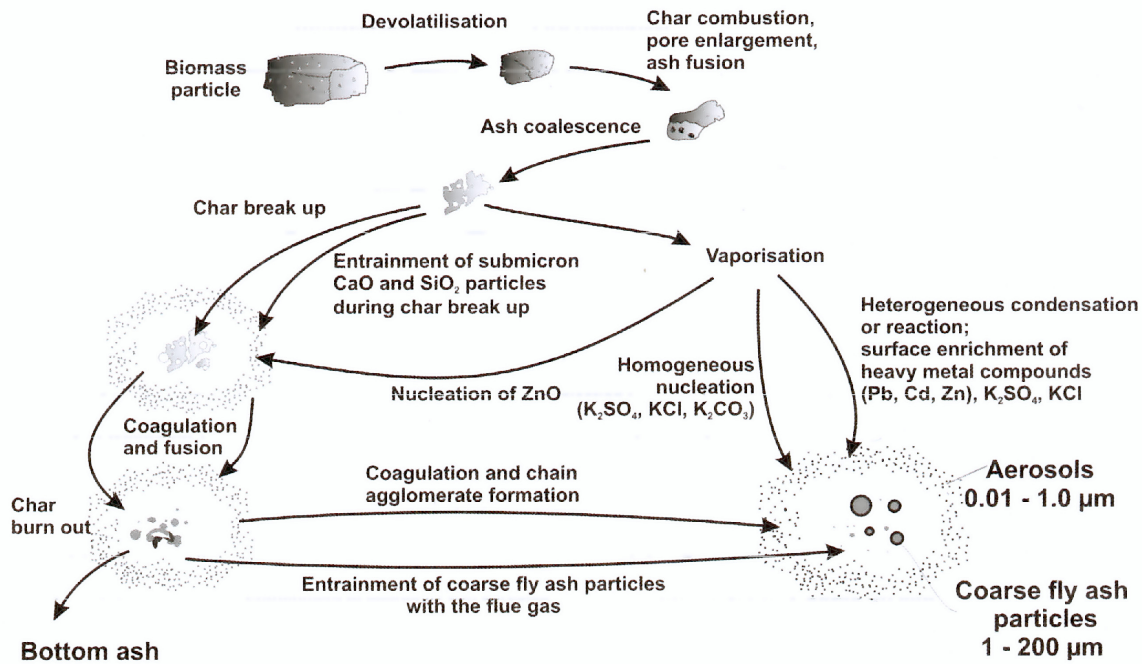


Figure 3. Schematic illustration of ash forming processes in biomass combustion (from Obernberger and Brunner [43])

1.5 Residential biomass fuels and appliances

Within the residential sector, biomass fuels are mainly used for heating or cooking purposes. Focusing on heating systems in the western world, different kinds of boilers, stoves and fireplaces is used with a considerable variety of models and designs. Residential appliances are traditionally and most often designed for the use of splitted and dried wood log fuels. Systems for small-scale wood chips or sawdust combustion are also available, although mainly used by farmers or in small central heating plants. Wood logs from both hardwoods (e.g. birch and oak) and softwoods (e.g. pine and spruce) are used depending on geographical conditions and local wood resources. Softwoods are also called conifers since they have cones. Hardwoods are generally denser than softwoods and therefore higher in energy content per equal volume of logs. Softwood often has higher pitch content which tends to burn with black smoke. Therefore, hardwoods are often considered to be a more "high quality" fuel than softwoods [22]. The importance of "good" fuel quality (i.e. the use of pure, properly dried and splitted wood logs) on the combustion performance is usually well-known, although not always applied. In Sweden, residential wood boiler system is commonly used for water-based heating and hot water production, preferably connected to a water accumulation tank to increase the comfort and combustion efficiency of the system. Significant shares of stoves and fireplaces is also in use, mainly as secondary heating source and the actual figure for the use and wood consumption in these appliance is rather uncertain. In other countries, different kinds of more or less advanced wood stoves and fireplaces for air-based heating are often more commonly used.

However, an increased use of biomass in the residential sector mainly lies on new technologies using upgraded biomass fuels. As discussed previously, the development of densified fuels (e.g. pellets) and appropriate combustion technologies have been considerable since the beginning of the 1980s. In Sweden, pellet production was initiated for large retrofitted powdered coal boilers but today also with a substantial use in the residential small-scale market. Presently, the raw materials for fuel pellet production are mainly stem-wood assortments (>90%) from sawmills and the wood working industry while bark, agricultural residues and other forest fuels only occasionally occurs [49]. Biomass pellets can be used in special burners adapted to existing wood or oil boilers. These types of pellet systems, which in many aspects resembles oil burners, have until today been the most commonly used pellet appliances for households in Sweden. In Austria and Germany, integrated pellet boilers are the dominating pellet boiler systems, although the basic construction and operating principles are similar for different boiler/burner systems [8]. In accordance with wood log heating systems, also stoves specially developed for pellets combustion is installed in increasing number. A pellet stove can preferably be used as primary heating sources replacing e.g. heating with electricity. Such pellets stoves have been the most common residential pellet system in countries like USA, and the market also in Sweden has increased significantly during the last 5-10 years. During the last decades, a significant development and increased variety of different residential pellet system has been seen, and a review on the state of the art of small-scale pellet based heating systems and relevant regulations was recently reported by Fiedler [8]. Emission regulations for these kinds of pellet appliances have been established during the last years, often focusing on the emissions of CO and dust (PM_{tot}) as well as OGC and NO_x in some cases, and the standards may differ somewhat between different countries. In Figure 4, schematic illustrations of typical residential pellets burner and stove system is shown.

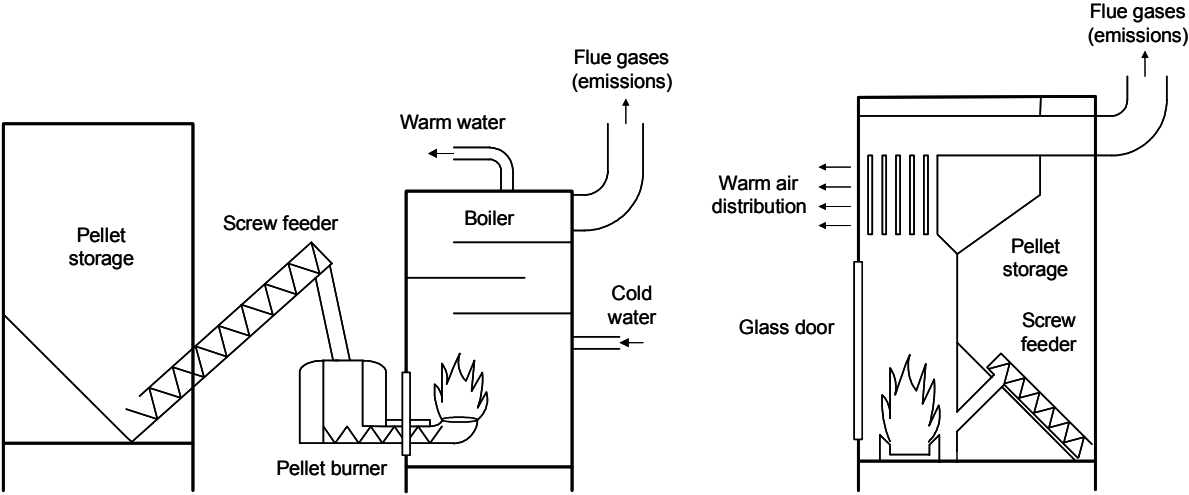


Figure 4. Schematic illustrations of typical residential pellet burner (left) and stove (right) systems.

1.6 Objectives and outline of the present work

The overall objective and outline of the work included in this thesis was to carefully and systematically study the emissions from small-scale residential biomass combustion appliances with respect to: i) experimental characterization and quantification, ii) influences of fuel, appliance and operational variables and iii) aspects of ash and trace element transformations and aerosol formation.

Special concern in the work was on sampling, quantification and characterization of particulate emissions during residential biomass combustion using different appliances, fuels and operating procedures.

The work includes seven separate papers with the following specific objectives to:

- I) initially review the scientific literature concerning adverse health effects from ambient air pollution in relation to residential wood combustion in modern society and if possible extract quantifications for the associations. (**Appendix I**)
- II) design a dilution sampling system (CVS) for emission measurements in residential biomass fired appliances and determine the influence of dilution sampling conditions on the characteristics and distributions of PM and PAH. (**Appendix II**)
- III) determine the mass size, elemental and inorganic phase distributions of particulate matter from residential combustion appliances using different pelletized woody biomass fuels. (**Appendix III**)
- IV) i) evaluate how different raw materials for pellets affect the accessibility of the existing burner equipment; ii) determine which of the ash forming element(s) that could be responsible for the deposit/slagging formation and; iii) estimate the critical slagging temperature for the different pellet raw materials. (**Appendix IV**)
- V) determine the characteristics and quantities of gaseous and particulate emissions from combustion in residential wood log and pellet stoves, and report emission factors for the most important emission components. (**Appendix V**)
- VI) determine the effects of temperature and residence time on the formation/destruction and characteristics of products of incomplete combustion, especially PAH, and particulate matter during combustion of conifer stem-wood pellets in a laboratory fixed-bed reactor (<5 kW). (**Appendix VI**)
- VII) i) determine whether the production process (i.e. drying procedure of the raw material) may be a source for enrichment of trace elements in wood pellets, ii) briefly evaluate the magnitude, relevance and relative importance of such potential enrichment and iii) evaluate some chemical equilibrium aspects of the behavior of relevant trace elements during production and use (combustion) of wood pellets. (**Appendix VII**)

2 Experimental, analytical and theoretical methods used

2.1 Gas analysis

2.1.1 Standard flue gases

In all experimental emission studies performed within the present thesis (**Paper II, III, V and VI**), the standard combustion flue gases (except SO₂), i.e. O₂, CO₂, CO, NO_x and TOC (total organic compounds) were measured. Standard gas instruments were used including an electrochemical sensor (Electra Control) and a paramagnetic sensor (M&C) for O₂, non-dispersive infrared spectroscopy (NDIR) (Maihak) for CO₂ and CO, chemiluminescence (EcoPhysics) for NO/NO_x and flame ionization detector (FID) (Jum Engineering) for TOC, also given as organic gaseous carbon (OGC).

2.1.2 Volatile organic compounds

In **paper V and VI**, volatile organic compounds were sampled in the flue gases, through a washing bottle to 10 L Tedlar bags. The bag samples were analyzed by direct injection in a Chrompack back-flush gas chromatography (GC) flame ionization detection (FID) system containing two different columns; i) a PLOT Al₂O₃/Na₂SO₄ column for identification of C₁-C₆ aliphatic compounds (i.e. alkanes and olefines) and ii) a CP-Wax 52 CB column for identification of (mono)aromatic volatile hydrocarbons. These VOC analyses were performed by Dr Esbjörn Pettersson at Energy Technology Centre in Piteå.

Samples of the extracted flue gases in the Tedlar bags were also injected through a Tenax-adsorbent for analysis mainly of C₆-C₉ aromatic volatile hydrocarbons, C₁₀ monoterpenes (wood log stove, **Paper V**) and C₈-C₁₀ alkanes (pellet stoves, **Paper V**). In some cases (pellet stoves, **Paper V**) samples were also injected through a Carboxpac-adsorbent to enable increased detection possibilities and accuracy for 1,3-butadiene. The identification and quantification of different VOC's were in this case made by using a GC-FID system equipped with thermal desorption/auto-injection (Perkin Elmer ATD 400). These VOC analyses were performed by IVL Swedish Environmental Research Institute Ltd in Gothenburg, although the results were evaluated by the author of the thesis and co-authors.

2.1.3 Polycyclic aromatic hydrocarbons

Sampling and analysis of gaseous (semi-volatile) and particulate polycyclic aromatic hydrocarbons was performed in **paper II, V and VI**. Particulate PAH emissions were collected on glass fiber filters (see 2.2.1 below) and polyurethane foam (PUF) plugs were used for sampling of the semi-volatile PAH. After a preparation procedure including e.g. washing, extraction and fractionation as described elsewhere [50, 51], the PAH fractions were analyzed by gas chromatography-mass spectrometry (GC-MS) for quantification as described in detail by Westerholm et al [52]. The extensive work concerning quantification and characterization of PAH was performed in close collaboration with Doc Roger Westerholm at Stockholm University, and a further summary of the sampling and analysis procedures is given in Appendix II, V and VI.

2.2 Particle sampling and measurements

2.2.1 Total PM sampling

Sampling of total particulate matter (PM_{tot}) was performed in **paper II, III, V, VI and VII** by using standard dust sampling equipment. A filter holder with dual filters (glass fiber or quartz) was in all cases used with subsequent possible analysis of: i) mass concentration (gravimetrically), ii) particulate bound PAH and/or iii) particle morphology and inorganic composition.

2.2.2 Low-pressure impactor

Different kinds of impactors are today commercial available and used for size selective sampling of airborne particles. The working principles of an impactor are based on inertial impaction and the system classifies the particles according to their aerodynamic diameter. To be able to determine the entire size distribution of an aerosol over a broad size range, a series of separate impaction stages are used in a cascaded way as shown in Figure 5. Beside mass size distribution, impactor sampling enables subsequent size fractionated chemical and morphological analysis. Depending on the sampling conditions, aerosol properties and potential analysis requirements, different material (e.g. aluminum, polycarbonate and quartz) and potential pre-treatment (i.e. greasing) can be used as sampling substrates in the impactor. A Dekati 13-stage low pressure cascade impactor (DLPI) [53] with the cut-off diameters range from 30 nm to 10 μm was used in the present work (**paper II, III, V, VI and VII**).

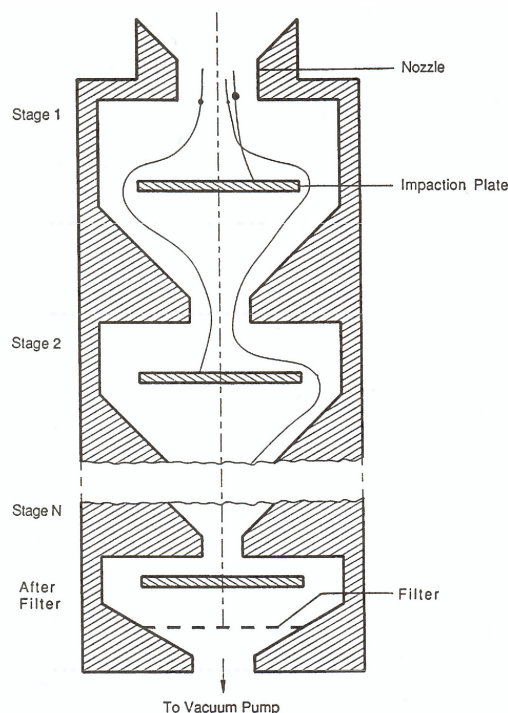


Figure 5. Schematic illustration of a cascade impactor similar to the Dekati LPI used in the present work (from Baron and Willeke [54]).

2.2.3 Scanning mobility particle sizer system

On-line measurements of fine particle mobility size distribution and concentration were performed by using a scanning mobility particle sizer (SMPS) system. These kinds of instruments are extensively used in a number of aerosol related applications, e.g. atmospheric science, nano-material processing, respiratory deposition and combustion science. A SMPS system consists of two separate instruments; a differential mobility analyzer (DMA) followed by a condensation particle counter (CPC). The DMA works as an electrical spectrometer which classifies particles according to their electrical mobility equivalent diameter (Figure 6). Before the DMA, a bipolar diffusion charger establishes an equilibrium charge distribution of the aerosol. By scanning the voltage in the aerosol flow field in the DMA, together with adjusting the flow rate conditions, size distributions within the range of 5-1000 nm can be covered for SMPS systems in general. In the CPC, single particles are detected (counted) optically by light scattering. Before detection, the aerosol passes a saturated n-Butanol vapor which after cooling makes the particles grow by condensation to approximately 10 μm .

In the present work, a SMPS system consisting of a DMA (model 3071A, TSI Inc, USA) and a CPC (model 3010, TSI Inc, USA), was used in **paper V and VI**. Since the particle number concentration in combustion flue gases normally exceeds the detection capacity of the CPC, the sample gas flow to the SMPS system was additionally diluted by two ejector diluters (Dekati Ltd, Finland) in series with dilution ratios between 7 and 8 in each dilution step.

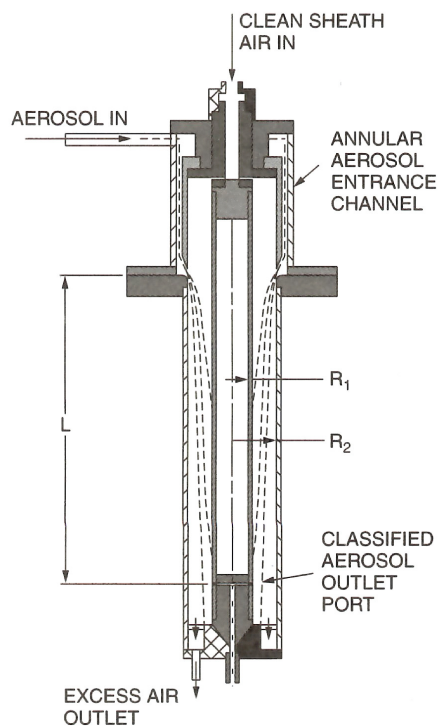


Figure 6. Schematic illustration of a cylindrical DMA similar to the TSI 3071 DMA used in the present work (from Baron and Willeke [49]).

2.3 Particle morphology and inorganic characteristics

2.3.1 *Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)*

Electron microscopy techniques are widely used to image the shape and structure (i.e. morphology) of solid surfaces or particles. By using the reflection (scattering) of electrons instead of light, as in ordinary microscopy, resolutions in the nanometre scale can be obtained. In the present work, an environmental scanning electron microscope (Philips XL30) was used on particulate samples (**paper III, V-VII**) as well as for slag samples (**paper IV**). The Philips SEM is also equipped with an EDAX energy-dispersive spectroscopy (EDS) detector, which is used for analysis of elemental composition of the sample by detection of X-rays emitted from the sample during subjection of electrons. These SEM analyses were performed at Energy Technology and Thermal Process Chemistry, Umeå University by the author of the thesis. Complementary microscopic analyses of fine particle samples were also performed in **paper V** by Per Hörstedt at the Department of Medical Biosciences, Umeå University using a Cambridge Stereoscan 360 IXP scanning electron microscope.

2.3.2 *X-ray powder diffraction (XRD)*

The structure and identification of crystalline phases can be determined by using powder X-ray diffraction (XRD). Applied on combustion research, XRD is an excellent analytical tool for inorganic characterization of different solid by-products, e.g. ash and particulate matter. In the present thesis XRD was used in **paper III and V** for characterization of the inorganic PM and in **paper IV** for characterization of slag samples. The XRD analyses were performed at Energy Technology and Thermal Process Chemistry, Umeå University by associate professor Dan Boström and the author of the thesis. A Bruker d8Advance instrument in θ - θ mode was used, with an optical configuration involving primary and secondary Göbel mirrors. The samples was mounted on a rotating low-background Si-single-crystal sample holder and by scanning the incident beam angle θ a complete range of reflections were obtained which enabled detection of different crystal configurations and layers (planes) present. Analyses of the diffraction patterns were done by Bruker software together with the PDF2 databank. In general, XRD is used extensively in our research to simultaneously obtain identification and semi-quantitative estimations of all crystalline phases present in ash or particulate samples.

2.3.3 *Additional inorganic analysis methods*

For some specific PM samples in **paper III**, X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) spectroscopy were used as complementary tools to SEM-EDS and XRD. These analysis methods can provide chemical structural information on a local structural level and were in this work used for possible further detailed chemical characterization of inorganic fine particles. The XPS analyses were performed by Dr Andrei Shchukarev at the Department of Inorganic Chemistry at Umeå University and the XAFS spectroscopy analysis were performed at Stanford Synchrotron Radiation Laboratory, California by professor Per Persson from the Department of Inorganic Chemistry at Umeå University. These methods were only of limited use in the present thesis, although with considerable relevance and potential for future chemical analysis of ashes and particulate emissions.

2.4 Chemical equilibrium calculations

Equilibrium calculations are generally used for interpretation of chemical processes regarding the fate and final products of different reactants. The use of chemical equilibrium models in high temperature chemical processes for energy production has been rather extensive since the 1960s [55]. There has been a continuous development and improvement of computer based modelling programs and thermodynamic databases such as FactSage [56], which is a fusion of the previous separate programs and databases in FactWin [57] and ChemSage [58]. The equilibrium calculation procedure in these programs as well as in many other today available chemical equilibrium modelling programs is based on the approach of minimization of the Gibbs free energy of the studied system.

The basis for the calculations can be illustrated by a hypothetical reactor (Figure 7), which can simulate either a whole combustion/gasification process (global equilibrium) or local conditions, for example in burning fuel particles or deposits on furnace walls.

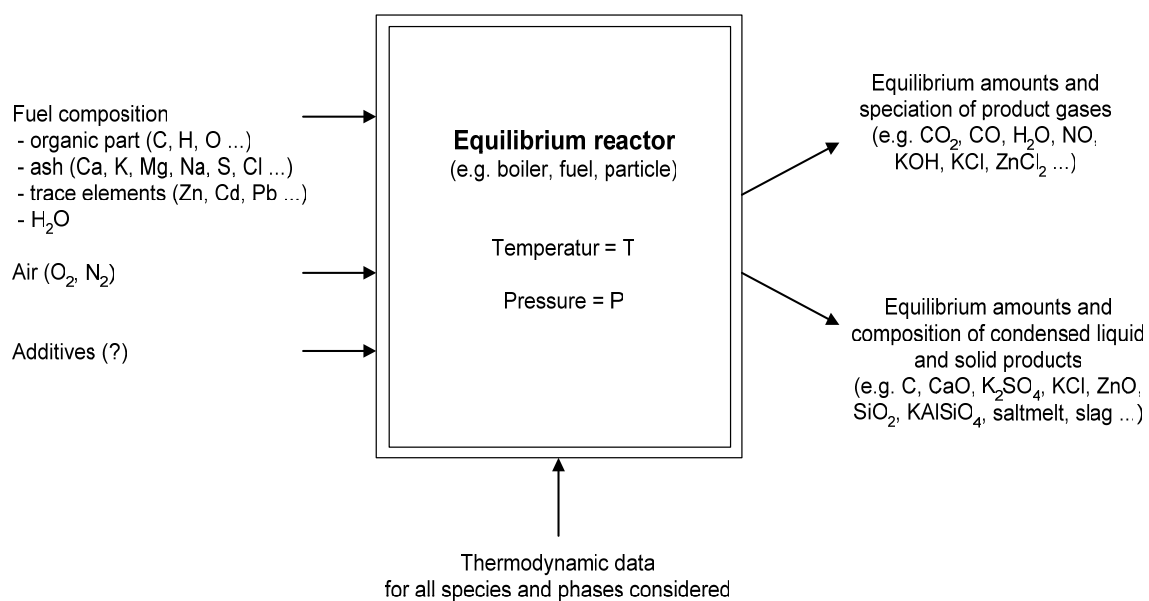


Figure 7. Illustration of a hypothetical equilibrium reactor and analysis approach.

In the present work, chemical equilibrium calculations were used to help interpret the experimental findings concerning i) the formation and phases composition of fine alkali aerosols (*paper III*), ii) the ash transformation processes and slag formation (*paper IV*) and iii) the behaviour of trace elements during combustion (*paper VII*).

3 SUMMARY OF CONTEXTS, EXPERIMENTAL PROCEDURES AND RESULTS

3.1 Health effects of residential biomass combustion - review (Paper I)

As discussed previously, the links between exposure to ambient air pollution and different adverse effects on human health have been extensively studied and documented and are in many aspects closely related to anthropogenic combustion processes [4]. Many questions still remain, though, e.g. how residential wood combustion (RWC) in modern society contributes to ambient concentrations of different air pollutants and the potential implications for human health. Therefore, a literature review of reported adverse health effects from ambient air pollution in relation to RWC in modern society was performed. The work focused on epidemiological studies from settings where RWC was mentioned as an important air pollution source. A significant number of animal toxicology studies with wood smoke have been performed and were reviewed by Zelikof et al [59] as well as a limited number of epidemiological studies previously reviewed by Larson and Koenig [7]. These and other relevant aspects of RWC, air quality and human health were also briefly summarized. From the literature search, nine relevant epidemiological studies were identified and summarized in Table 1, all focused on effects of short-term exposure such as asthma admissions, respiratory symptoms, daily mortality and lung function.

Table 1. Summary of addressed health effects and brief results from the reviewed papers. The reference numbers in the table refers to the references in the full article (Appendix 1).

Effect	Reference	Subjects age	Pollution indicators	Significant positive associations with
Daily mortality	38	all ages	PM ₁₀ , SO ₂ , CO, NO _x	PM ₁₀
Asthma symptoms	39	5-13 years	PM ₁₀ , PM ₁ , SO ₂ , CO	PM ₁₀ , PM ₁ , CO
Asthma hospital admissions	40	< 65 years	PM ₁₀ , PM _{2.5} , CO, SO ₂ , O ₃	PM ₁₀ , PM _{2.5} , CO, O ₃
	41	< 18 years	PM ₁₀ , PM _{2.5} , CO, NO ₂	PM ₁₀ , PM _{2.5} , CO
Asthma emergency room visits	36	all ages	PM ₁₀ , NO ₂ , O ₃ , CoH	PM ₁₀
	43	all ages	PM ₁₀ , SO ₂ , O ₃	PM ₁₀
Peak expiratory flow and respiratory symptoms	35	children	PM ₁₀	PM ₁₀ (in asthmatics)
	42	> 55 (COPD)	PM ₁₀ , SO ₂ , CO, NO ₂	PM ₁₀ , NO ₂
Forced expiratory volume in 1 sec and forced vital capacity	37	children (grade 3 to 6)	Fine particulate, PM _{2.5}	PM _{2.5} (in asthmatics)

Substantial quantitative information was only found for acute asthma in relation to particulate matter with an aerodynamic diameter of <10 µm (PM₁₀). In comparison with the present general estimations for ambient PM and adverse health effects [60, 61, 62] the relative risks are even stronger in the studies where residential wood combustion is considered as a major PM source (Figure 8). Thus, there seem to be at least no reason to assume that the PM effects in wood smoke polluted areas are weaker than elsewhere. Ambient exposure to combustion related fine particles in general have also been associated with cardiopulmonary disease and mortality as well as cancer risks, but the importance of other particulate

properties than mass concentration, like chemical composition, particle size and number concentration remain to be elucidated.

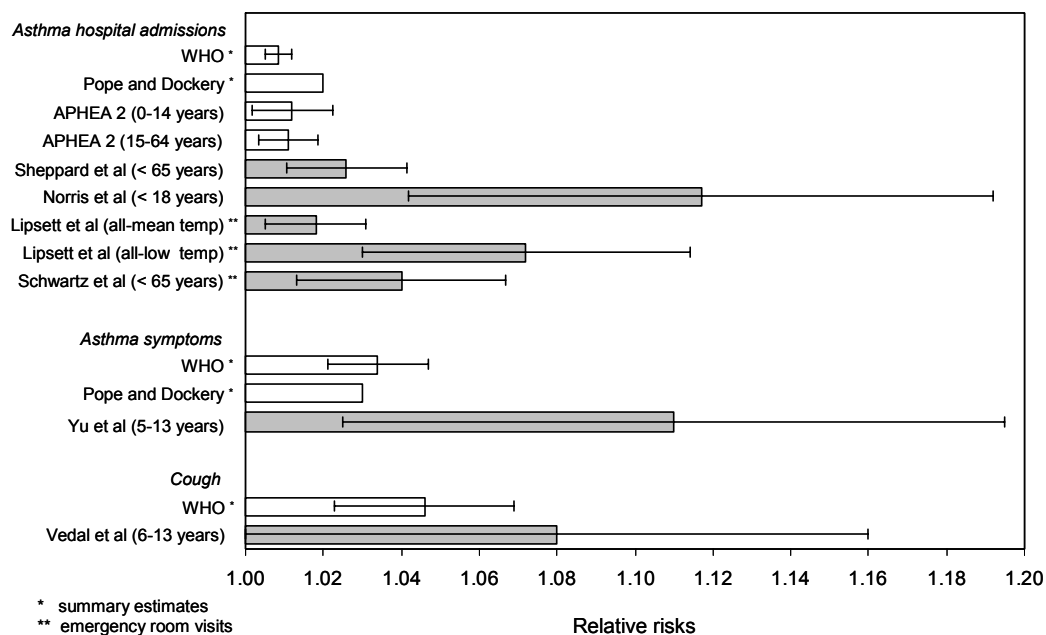


Figure 8. Relative risks for different morbidity outcomes associated with a $10 \mu\text{g}/\text{m}^3$ increase in PM_{10} (particulate matter with an aerodynamic diameter $<10 \mu\text{m}$) with 95% confidence intervals as error bars. Studies where wood smoke was considered as a major air pollution source are shown by closed columns, and comparison estimates are represented by open columns. Detailed reference information is given in the full article (Appendix I).

3.2 Emission dilution sampling for residential appliances (Paper II)

To be able to perform relevant health impact assessments, set appropriate regulatory standards and make accurate evaluations of different combustion devices, detailed emission characterization and identification of relevant components is needed. Traditionally, emission sampling have been performed in undiluted, hot ($120\text{-}180^\circ\text{C}$) flue gases which in some aspects suffers from drawbacks for example related to transient conditions with varying flue gas flows and the condensable nature of many of the semi-volatile organic compounds. Sampling at lower temperatures and under constant flow conditions is therefore desirable. The most extensively used and generally applicable method is based on whole flow dilution in a dilution tunnel where a constant flow of diluted flue gases enables constant volume sampling (CVS). The methodology of CVS system was first designed for gasoline fuelled vehicles in the beginning of the 1970's [63] and has then been used and evaluated extensively. While this kind of dilution sampling has become the standard reference method for internal engine emission measurements, the experiences of such methods for stationary sources and solid fuel combustion are more limited although some work have been performed. A dilution sampling system for residential wood stove emissions has for example been defined and used by US EPA [64] and a similar standardized dilution tunnel method has been used for determination of particulate emissions from residential wood stoves and

furnaces in Norway [65]. There is, however, still a need for detailed characterization and quantification of the emissions, not the least concerning particulate matter and PAH, under controlled and standardized conditions, using different fuels and combustion techniques.

An appropriate CVS system (Figure 9) for residential biomass combustion appliances was therefore designed, constructed and evaluated. The effects of sampling conditions on the characteristics and distribution of PM and PAH as well as concentrations of CO, OGC and NO, were studied according to factorial experimental designs [66, 67] and were evaluated by PLS regression analysis [68, 69]. Robust and optimal sampling variable settings for the sampling method were also determined. Dilution ratio (3-7), sampling temperature (45-75°C) and dilution tunnel residence time (1-3 s) were varied during combustion of typical softwood pellets combusted in a residential stove. Sampling of PM_{tot} and particulate PAH was performed in the dilution tunnel using glass fiber filters for particulate PAH with subsequent PUF plugs for semi-volatile PAH. Particle mass size distributions were determined by using a 13-stage LPI (0.03-10 µm).

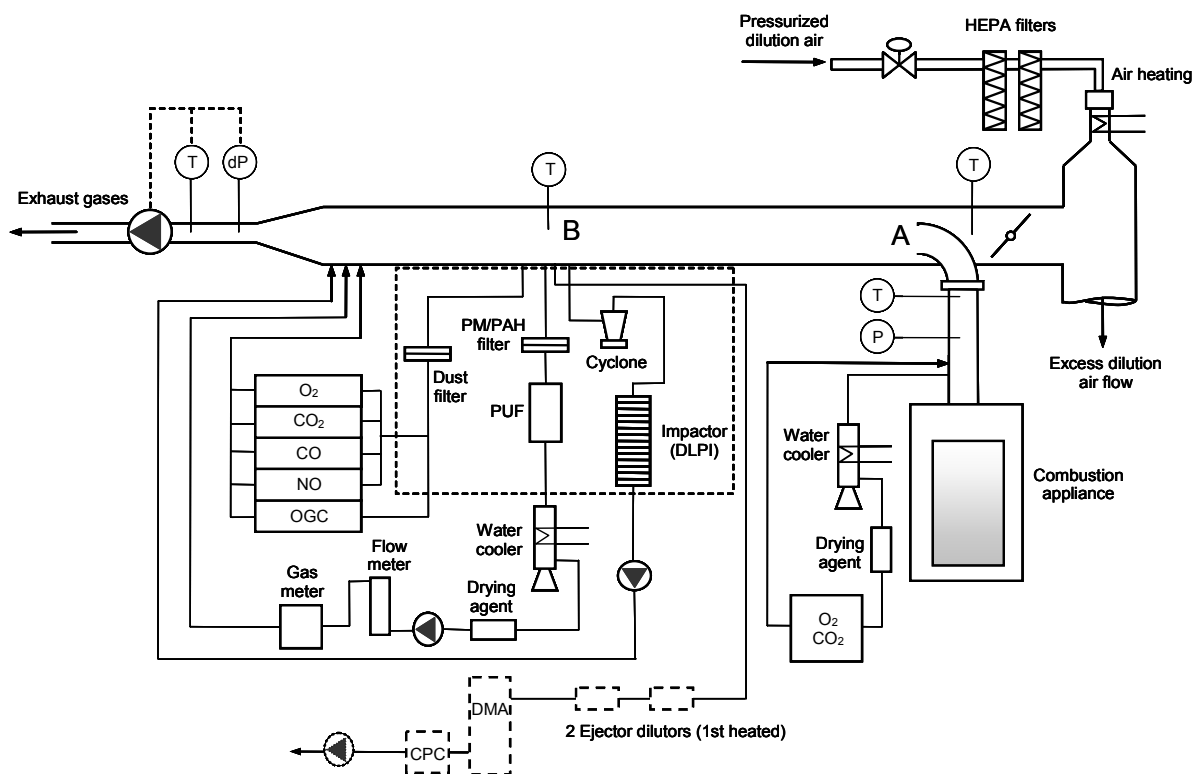


Figure 9. Schematic illustration of the experimental dilution set-up for constant volume sampling (CVS). In the present study the distance between the mixing point (A) and sampling probes (B) were varied between 0.5 and 3.0 m and the temperature of the equipment for PM and PAH sampling (within the dashed line) were varied between 45 and 75°C according to the experimental designs. Sampling hose for OGC was heated to approximately 150°C. The SMPS (DMA+CPC) system was not used in the present evaluation study (**Paper II**) but in the following emission studies (**Paper V and VI**).

The emissions of PM_{tot} were in the range of 11-20 mg/MJ and 32-81 mg/MJ at high and low load respectively, totally dominated by fine (<1 µm) particles. MMD of the fine mode varied in the range of 117-146 nm. No influence of sampling conditions was determined for PM_{tot} or

MMD. The distribution between particulate and semivolatile phase was influenced for 12 of the 37 analyzed PAH compounds, mainly by increased fractions of semivolatile material at higher sampling temperature. No influence of the variations in sampling temperature studied (45-75°C) was, however, observed for the concentration of PAH_{tot}, or the dominating PAH compounds, i.e. phenanthrene, fluoranthene and pyrene. This indicated that the recovery of the sampling method for PAH was unaffected by the variations in sampling temperature studied. Variations in residence time had no significant effect on any studied emission parameter. The different PAH compounds were divided into four groups according to their specific distribution between particulate and semivolatile phase during different sampling conditions (Table 2).

Table 2. Summary of the 37 analyzed PAH compounds and their distribution between particulate and semivolatile phase during different sampling conditions. In increasing order sorted by molecular weight within each group respectively.

Always found as particulate bound	Always found in semi-volatile phase	Influenced by sampling conditions ^a	Not detected in any case
Dibenzothiophene	2-Methylfluorene	Fluorene	9-Methylanthracene
9,10-Dimethylanthracene	3,6-Dimethylphenanthrene	Phenanthrene	Indeno(1,2,3-cd)fluoranthene
Benz(a)fluorene		Anthracene	Dibenz(a,h)anthracene
2-Methylpyrene		3-Methylphenanthrene	
4-Methylpyrene		2-Methylphenanthrene	
1-Methylpyrene		2-Methylanthracene	
Benzo(ghi)fluoranthene		9-Methylphenanthrene	
Benzo(c)phenanthrene		1-Methylphenanthrene	
Benzo(b)naphto(1,2-d)thiophene		2-Phenylnaphthalene	
Cyclopenta(cd)pyrene		3,9-Dimethylphenanthrene ^b	
Benzo(a)anthracene		Fluoranthene	
Chrysene		Pyrene	
Benzo(b+k)fluoranthene			
Benzo(e)pyrene			
Benzo(a)pyrene			
Perylene			
Indeno(1,2,3-cd)pyrene			
Benzo(ghi)perylene			
Coronene			

^a Sampling temperature had the major influence on the distribution for all 12 compounds, i.e. increased sampling temperature yielded less PAH material as particulate bound.

^b Almost always found as particulate bound

The conditions and variations in the presently studied CVS system with a lower dilution ratio and somewhat longer residence time than what has been suggested for vehicle emissions [70] are probably appropriate to more closely simulate the conditions for residential combustion emissions. To minimize potential recovery losses (i.e. low temperature without water condensation) and maximize the detection possibilities (i.e. lowest necessary degree of dilution), sampling at 50±5°C with a dilution ratio of 3-4 times was suggested as robust and applicable sampling conditions in the present emission sampling set-up. The need for combined sampling of gaseous and particulate bound PAH was also clearly illustrated. Overall, the present CVS system for residential biomass combustion appliances was constructed, evaluated and shown to be an appropriate dilution sampling set-up used in the following emission studies (**Paper III, V and VI**).

3.3 Inorganic PM of different pelletized woody raw materials (**Paper III**)

The characteristics and properties of emitted particles are important for the fate in the atmosphere and environment as well as potential biological responses following human exposure. Concerning the links between exposure to combustion related particulate matter and human health, the importance of other particle properties than mass concentration, e.g. chemical composition, particle size and number concentration, has been emphasized [17, 71, 72]. Presently, the raw materials for fuel pellet production are mainly stem-wood assortments (>90%) from sawmills and the wood working industry while bark, agricultural residues and other forest fuels only occasionally occurs [9] However, with an increasing utilization of the forest resources, other types of wood based materials (e.g. bark and logging residues) might be used for pellet production. Compared to ordinary stem-wood, these raw materials have a broader variation in the total fuel ash content as well as in the amount of different ash forming elements [73]. Such change in ash content and composition can significantly influence the ash transformation processes that could increase the occurrence of potential ash related operational problems and affect the formation and characteristics of inorganic particulate matter emissions. The behavior of the inorganic ash material during combustion of different pelletized woody raw materials in residential pellet burners were therefore studied with respect to i) inorganic PM characteristics (**Paper II**) and ii) silicate formation, alkali capture/release and potential ash related problems (**Paper III**).

In the part of the work concerning PM characteristics (**Paper III**), the mass size, elemental and inorganic phase distributions of the particulate emissions were experimentally determined. Six different pellet fuels of fresh and stored (6 months) softwood sawdust (S0/S6), logging residues (L0/L6) and bark (B0/B6), in detail describe elsewhere [74], were combusted in three commercial pellet burners (10-15 kW). The burners (A, B and C) represented different types of burner constructions with overfeeding, horizontal feeding and underfeeding of the fuel. The experiments were performed using the previously described dilution sampling set-up (**Paper II**). Particle mass size distributions were determined using the 13-stage LPI (0.03-10 μm) with a pre-cyclone. The PM was analyzed for morphology (using ESEM), elemental composition (using EDS) and crystalline phases (using XRD). Selected impactor samples were also analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) spectroscopy. In addition, chemical equilibrium model calculations were performed with the program FACT-Win 3.05, divided in two steps to study; i) volatilization of ash forming elements in the temperature range of 900-1100°C and ii) condensation behavior of volatilized material during cooling of the flue gases.

The emitted particles were mainly found in the fine sub-micron mode with mass median aerodynamic diameters between 0.20 and 0.39 μm , and an average PM_{10} of $92 \pm 6.2\%$. Minor coarse mode fractions (>1 μm) were present primarily in the experiments with bark and logging residues. In Figure 10, ESEM micrographs of three typical particle types identified are shown.

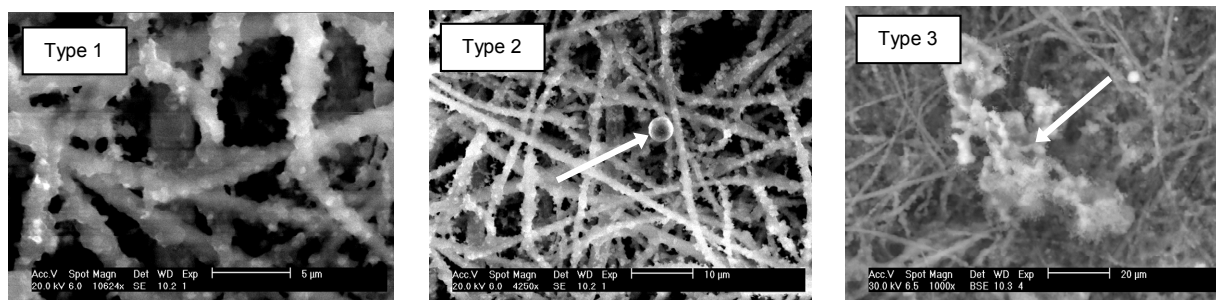


Figure 10. ESEM images of total PM samples on quartz fiber filters, showing three different typical particle types that could be identified; 1) fine sub-micrometer sized particles/aggregates 2) spherical coarse particles and 3) irregular aggregated coarse particles.

Relatively large and varying fractions (28-92%) of the PM were determined to be products of incomplete combustion. The inorganic elemental compositions of the fine particle samples were dominated by K, Cl and S with minor amounts of Na and Zn (Figure 11). The relative distribution of these five elements within the fine mode in the different cases was rather homogeneous, only with a small trend of increased sulfur content with increased particle sizes in some cases (Figure 12). The dominating alkali phase identified was KCl with minor but varying amounts of $K_3Na(SO_4)_2$ and in some cases also K_2SO_4 .

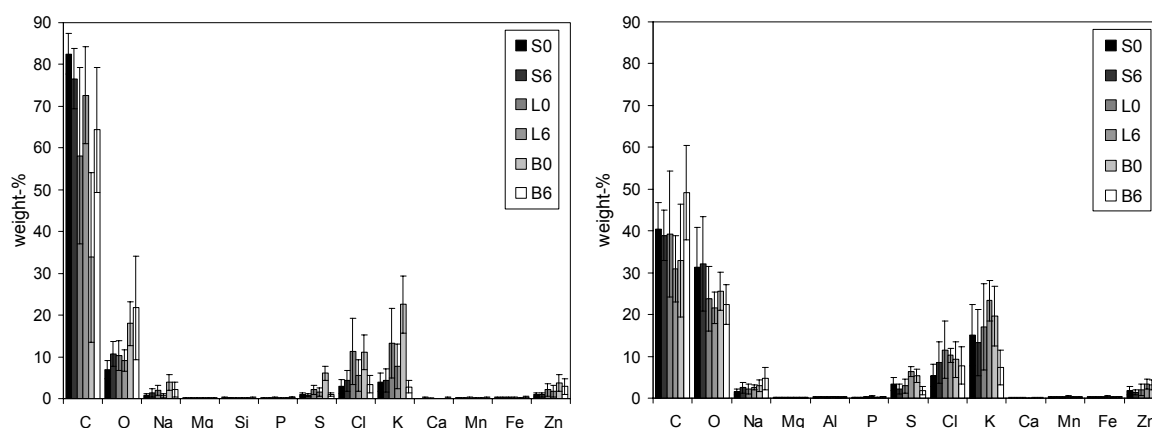


Figure 11. Elemental composition of the fine PM from burner B (left) and burner C (right). Standard deviations within the fine mode (different LPI stages) are shown as error bars. For burner B (using Al-foils) Al was excluded from the analysis, and for burner C (using quartz fiber filters) Si was excluded.

The results further indicated zinc to be almost fully volatilized in the reducing atmospheres of burning fuel particles, subsequently forming or condense on fine (<1 μm) particles. No identification of any zinc containing phase could be made by XRD. However, both XPS and XAFS spectroscopy undoubtedly identified Zn-O interactions, where oxygen atoms most possibly derive from ZnO or $Zn(OH)_2$, but some also potentially from anions like SO_4^{2-} or CO_3^{2-} . The XAFS analysis also revealed distinct Zn-Zn interactions as well as interactions between Zn and some possible anion, presumably Cl^- or SO_4^{2-} or CO_3^{2-} . Therefore, the concise chemical information indicated the presence of a more complex solid zinc containing phase than pure zinc oxide or some simple zinc salt. Accordingly, the formation mechanism and exact phase composition of zinc containing particles during biomass combustion in different applications still remain to be elucidated.

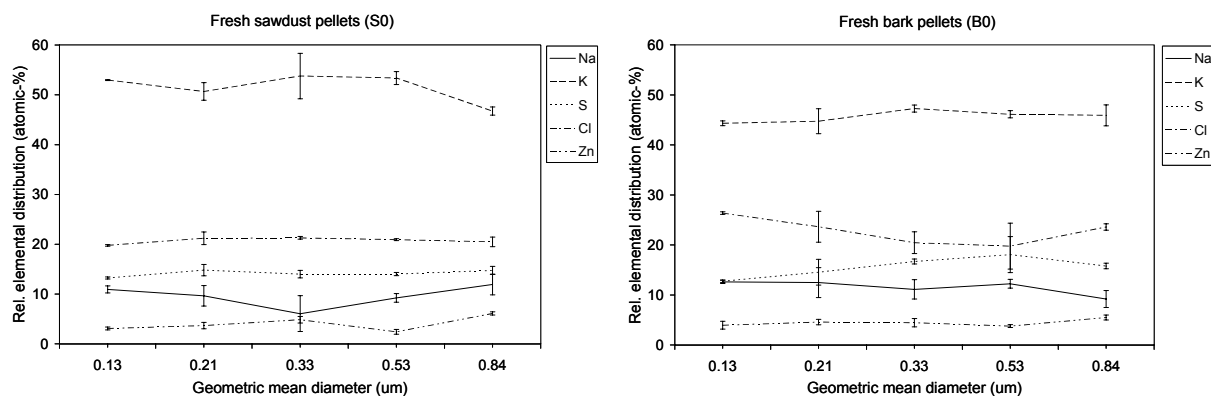


Figure 12. Typical relative elemental distributions of the five elements present within the fine mode on a carbon and oxygen free basis, illustrated by the results during combustion of pelletized softwood sawdust (left) and bark (right) in a residential burner. The average distribution (in atomic-%) is shown for each impactor substrate number 3-7 (0.13-0.84 μm) with standard deviations as error bars.

With some constraints, the results also showed that the relative amounts and phase composition of the alkali containing PM seemed to be quite similar to what was predicted by chemical equilibrium. As seen in Figure 13 (left), the degree of volatilization of potassium as the main aerosol forming element highly influenced within the temperature interval relevant for residential pellet burners. A significant but varying alkali silicate (slag) formation was both experimentally determined and theoretically predicted which is more thoroughly discussed in *Paper IV*. Since potassium was the major ash forming element in the fine inorganic particulates, the fate and potential capture in the bottom ash is of vital importance for the formation of alkali containing aerosols during combustion of biomass. Further in Figure 13 (right), the calculations typically predicted KCl and K_2SO_4 to be the major condensed phases in the fine PM. Also $\text{K}_3\text{Na}(\text{SO}_4)_2$ (Aphthitalite), a solid solution thermodynamically stable up to a maximum 470°C [75] and experimentally identified by XRD, was predicted by the equilibrium calculations.

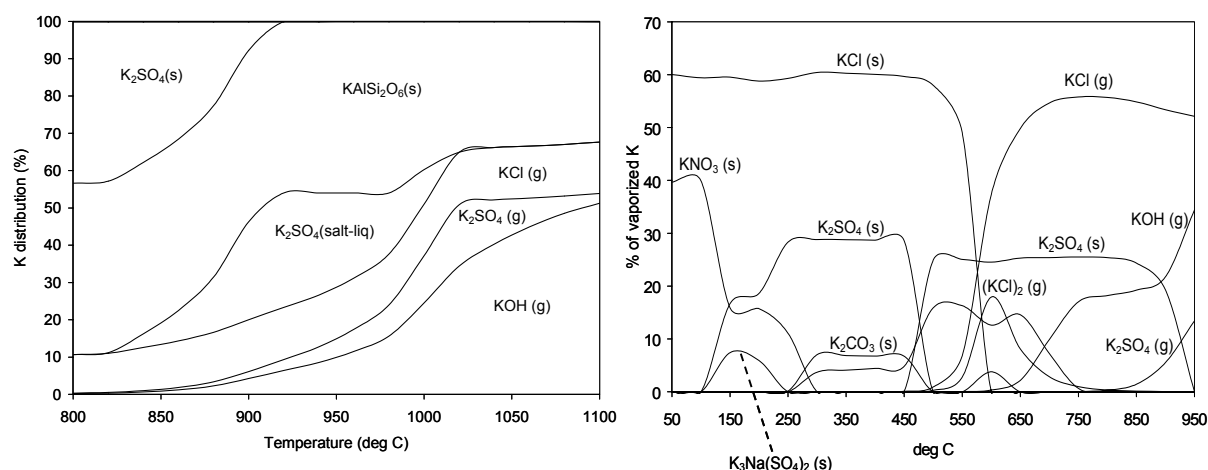


Figure 13. Typical predicted distribution between gaseous and condensed phases for potassium (left) and equilibrium diagram during cooling of the volatilized potassium (right) during combustion of softwood sawdust.

3.4 Ash transformation, alkali capture and potential ash related problems (Paper IV)

As discussed previously (*Paper III*), the behavior of the alkali elements is of vital importance for the ash transformation processes and formation of fine particles during combustion. Beside the influence on PM formation and characteristics, the amount and composition of the ash forming matter in different fuels is also of great concern regarding potential ash related operational problems. In general, combustion of pellets in automated and optimized systems provide possibilities of more user friendly operation with higher combustion efficiency and emission performance compared to traditional wood log firing [76, 77]. However, the use of other wood forest based and ash rich materials than pure stem-wood assortments will increase the importance of a basic understanding of the chemical processes that govern the formation and distribution of ash forming matter. The stability, preferred equilibrium distributions and kinetically reachable compositions also directly control the volatilization of fine particle forming materials.

The ash transformation, alkali capture and potential related problems (i.e. slagging tendencies) were therefore experimentally studied when pellets of different woody raw materials were combusted in different residential burners (A, B and C). As mentioned earlier, the experimental part was closely coordinated with the work on PM characteristics presented in *Paper III*, using softwood sawdust, logging residues and bark, respectively, as well as "reference" conifer stem-wood pellets. Each test run lasted for about 36 h corresponding to 35-40 kg burned pellets. The amount of ash, slag and deposited fly-ash in the boiler were determined. The slag deposits were visually classified in four categories with subsequent chemical characterization by XRD, ESEM-EDS and ICP-AES. Controlled sintering tests of collected slag samples for determination of critical sintering temperatures were also performed in a bench scale fluidized bed furnace according to a method described more thoroughly elsewhere [78, 79]. In accordance with the study of inorganic PM, chemical equilibrium calculations were used to interpret the experimental findings, in this case to predict the ash transformation processes and sintering tendencies in the range of 800-1100°C.

Overall, the results clearly indicated that the actual performance and ash transformations were very close to what was predicted by chemical equilibrium. A significant formation of relatively potassium rich slag was formed for all tested burners during combustion of all studied fuels and the fraction of fuel ash that formed slag was relatively similar for all studied fuels, except B6 (significantly more) and Sref (no measurable amount). The major part of the slag formed consisted of crystalline material of Ca/Mg-silicates, K/Al-silicates and SiO₂ in different proportions, with minor amounts of amorphous (glassy) material. Minor amounts of P, Mn, Fe and Na was also found in the slag whereas S and Cl was totally depleted from the slag.

A relatively good correlation between the content of silicon and the fraction of fuel ash that forms slag in the burners (sintering tendencies) were found. Accordingly, the present work

therefore seems to confirm that melt formation of “sticky” low temperature melting silicates is responsible for the slag (silicate) formation. Based on the present and previous work, suggestions of the chemical/physical sub-processes governing alkali release, capture and slag formation were made including an initial release of alkali metals into the gas-phase (e.g. KOH, KCl and NaCl) with subsequent reactions with organically or mineral bound silicon and formation of silicate melts. Thus, the processes govern the silicate formation influences the transformation and release of alkali metals to the gas phase and subsequent fine particle forming fraction. From the analysis of fuel ash and slag samples it was further estimated that $15\pm 12\%$ (1.4-40) of the total amount of K was captured as silicate melts, i.e. slag.

The drastically increased content of silicon determined in the stored bark, most probably derived from soil and dust contamination of the fuel during handling, storage, drying or pelletizing. An interesting and important observation was also that, in contrast to the reference pellets, formation of silicate slag occurred during combustion of the two stem-wood assortments, although not in the same degree and with severe consequences as when using bark or logging residues. This was most probably caused by a contamination of the stem-wood raw material in the processing of the pellet fuels, which influences the ash transformation processes during combustion. The reasons for the slagging during stem-wood pellet combustion and some measures for prevention is discussed more thoroughly in a parallel work presented elsewhere [80] and the potential contamination (enrichment) of trace elements in the pellet production process is also discussed further later in this thesis (*Paper VII*).

A consequence of the present results is that relatively moderate reductions of temperatures in the appliances (i.e. on the burner grates) should most probably reduce the potential slagging and sintering tendencies during combustion of ash rich woody biomass pellets. Such reduction of combustion temperature may, however, influence the combustion conditions and emission performance with potential increased formation of PIC's. Another possibility for prevention of slag formation during biomass combustion is by adding sorbents in the fuel or combustion process. In a recent work, it was shown that the formation of low-temperature-melting K-silicates can be prevented or significantly reduced by introduction of fuel additives (e.g. kaolin and limestone) in the pellets [81]. Previous studies have also illustrated the potential for capturing trace metals by injection of different sorbent additives (e.g. kaolinite) in high temperature combustion environments [82]. Accordingly, the potential multiple positive effects of specific fuel additives is highly interesting to consider in different biomass combustion applications, not at least during combustion of pelletized biomass fuels in small-scale appliances.

3.5 Gaseous and particulate emissions from wood log and pellet stoves (Paper V)

It is rather well documented that residential wood combustion can be a major source of health relevant air pollutants like hydrocarbons (e.g. VOC and PAH) and particulate matter in urban environments [6, 7, 83]. The emissions from different kinds of residential biomass systems can, however, vary significantly both qualitatively and quantitatively, depending on a number of factors, e.g. appliance type, fuel properties and operation [76, 84, 85]. Despite the previously well documented extent and importance of these pollution sources and components, relatively limited information is, however, available concerning detailed emission characteristics and quantification for different appliances and fuels.

Therefore, the characteristics and quantities of gaseous and particulate emissions from combustion in residential wood log and pellet stoves were determined and emission factors for the most important emission components reported in an extensive experimental study. A large number of gaseous and particulate components were studied for wood log and pellet stoves with systematic variations in fuel, appliance and operational properties. Beside the standard flue gas components, i.e. O₂, CO₂, CO, TOC (total gaseous organic compounds) and NO/NO_x, the emissions of 34 specific VOC's and 43 specific PAH's were measured. Particulate sampling included PM_{tot} filter sampling (mass concentration), a low-pressure cascade impactor (LPI) (mass size distribution) and a scanning mobility particle sizer (SMPS) system (fine particle number size distribution and concentration).

Birch wood logs were combusted in a wood stove under different simulated operation conditions (modes) and the results were compared to when logs of pine and spruce were used as fuels. Special focus was on detailed characterization of the emissions of hydrocarbons (i.e. VOC and PAH) as well as the particulate matter. Two conifer sawdust pellets (6 and 8 mm in diameter) were further combusted in two different pellet stoves with systematic variations in chimney draught and fuel load.

Considerable variability of emission performance in the wood log stove was determined, with potentially very high emissions of products of incomplete combustion (PIC's) during specific conditions (Figure 14). However, by proper technical and/or operational measures, the emission performance can be well controlled and a significant potential for further development and optimization therefore exists.

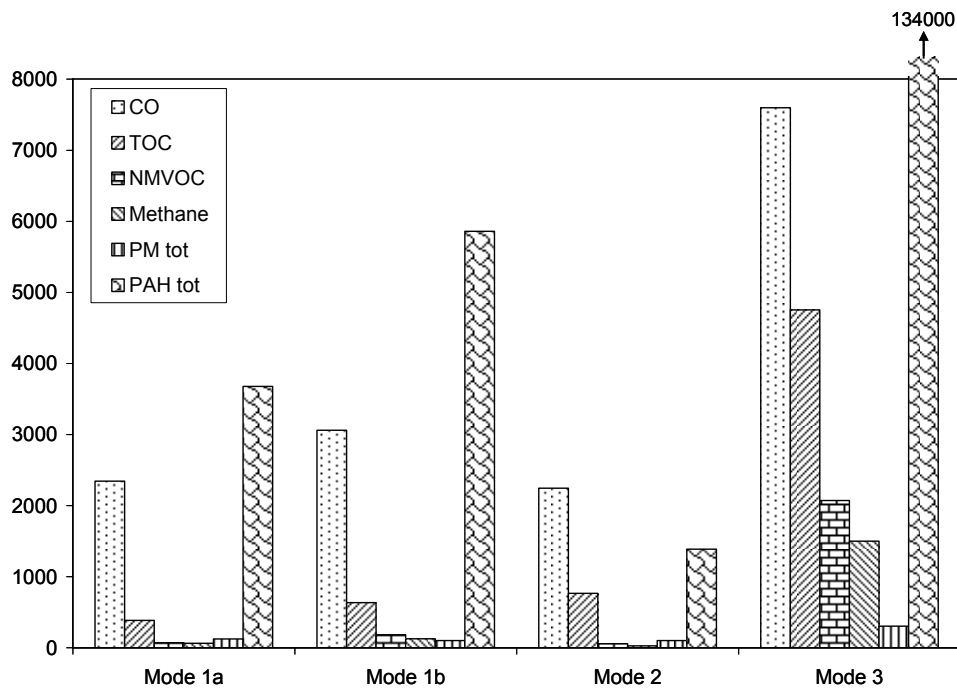


Figure 14. Comparison between the average emissions of the main components from the wood stove during different operation modes, given as mg/MJ (PAH given as $\mu\text{g}/\text{MJ}$). TOC given as CH_4 -equivalents. The conditions in the different modes aimed to simulate; Mode 1 (a) = "Normal" stove and fuel conditions (2 experiments with birch wood), Mode 1 (b) = "Normal" stove and fuel conditions (2 experiments with conifer wood), Mode 2 = "Cold and air starved" combustion with moist and large logs (2 experiments with birch wood), Mode 3 = "Intensive" combustion with high draught and extra dry and cleaved logs (2 experiments with birch wood).

The emissions of PIC's as well as PM from the wood log stove were generally considerably higher than from the pellet stoves. Accordingly, the use of up-graded biomass fuels with controlled combustion conditions gives advantageous conditions for optimization of the combustion process compared to traditional batch wise firing of wood logs. There is, however, still a potential for further minimization of PIC emissions in residential pellets applications, especially at low loads.

Beside methane which was the major VOC in all cases, ethene, acetylene and benzene were the most dominant VOC's and the dominating PAH's were in all cases phenantrene, fluoranthene and pyrene.

Fine sub-micron particles dominated in all cases the PM with 80-95% as PM_{10} . The minor coarse fraction consisted of carbonaceous unburned fuels residues with inclusions of calcium containing grains (1-10 μm) (Figure 15).

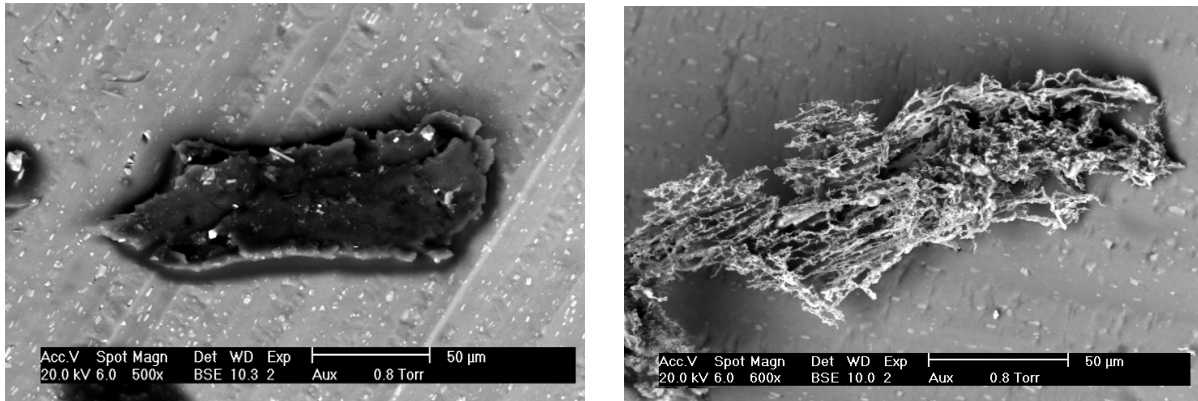


Figure 15. SEM images of typical coarse mode particles sampled with the PM8-cyclone during combustion in the wood log and pellet stoves. Left image shows a typical particle found both in the emissions from wood log combustion and pellets combustion. The right image shows a second type of carbonaceous coarse particle found in the emissions during the start-ups with pellet stove B.

Fine particle mass median and count diameters were in the range of 100-300 nm and 50-250 nm respectively with number concentrations at $4.6 \cdot 10^{12}$ - $1.1 \cdot 10^{14}$ /MJ (Figure 16-18).

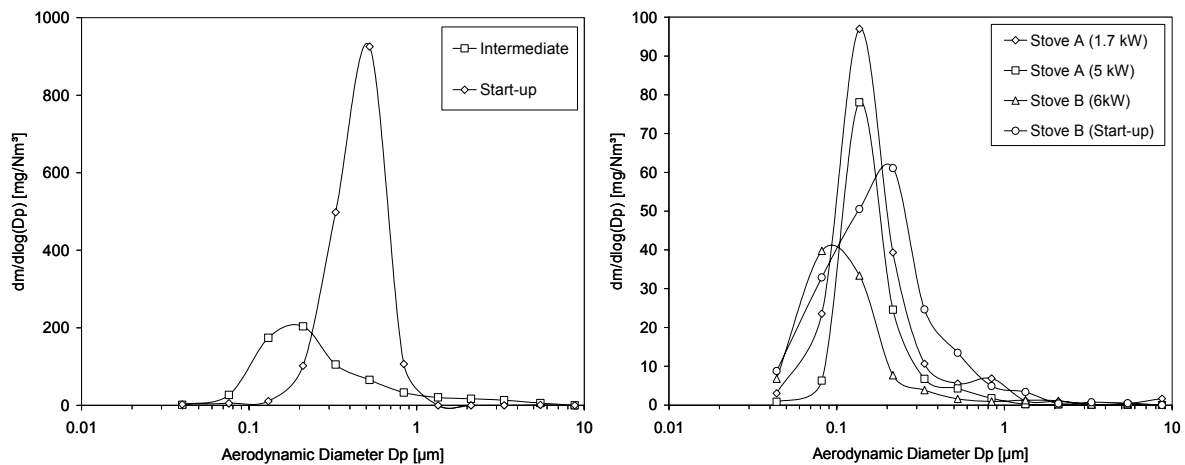


Figure 16. Typical particle mass size distribution for the wood log stove (left) and pellet stoves (right), measured by the LPI. Upper impactor stage and pre-cyclone not included. (concentrations are normalized to 10% O₂)

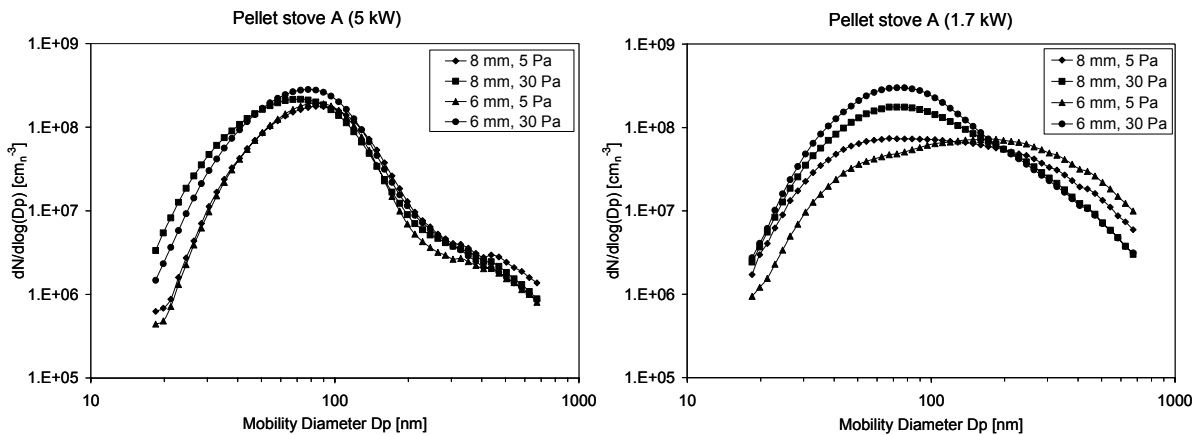


Figure 17. Average fine particle number size distributions for one of the pellet stoves measured by the SMPS. For each case, the size distributions during experiments with variations in pellet fuels (6 and 8 mm) and chimney draught (5 and 30 Pa) are included.

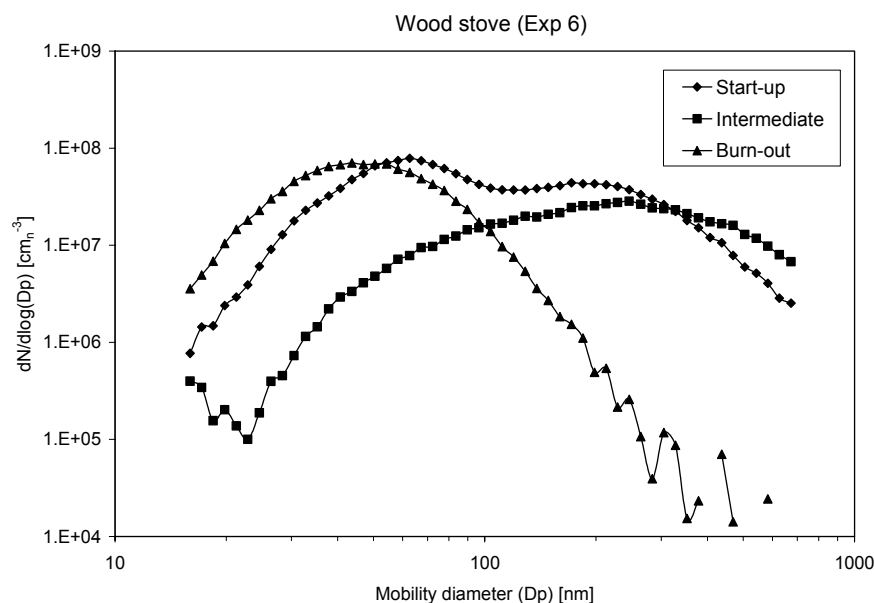


Figure 18. Typical average fine particle number size distributions for the wood stove during different phases of a combustion cycle, measured by the SMPS. The tail of the intermediate distribution below 25 nm is most probably an artefact of the operation (ventilation) of the CPC. (concentrations normalized to 10% O₂)

The emissions of PM_{tot} varied in the range of 35-350 mg/MJ for the wood log stove and 15-45 mg/MJ for the pellet stoves. Previous studies of "optimized" combustion of softwood pellets with almost a total depletion of PIC's have shown that the emissions of inorganic PM are in the range of 15-20 mg/MJ [86] (**paper VI**). Assuming similar ash composition and volatilization conditions therefore confirms that the PM from the wood stove experiments were dominated by PIC's (i.e. carbonaceous material) which also was illustrated by the high content of carbon detected by SEM/EDS in the fine PM. The elemental composition of the fine PM from the birch wood combustion is shown in Figure 19a and b.

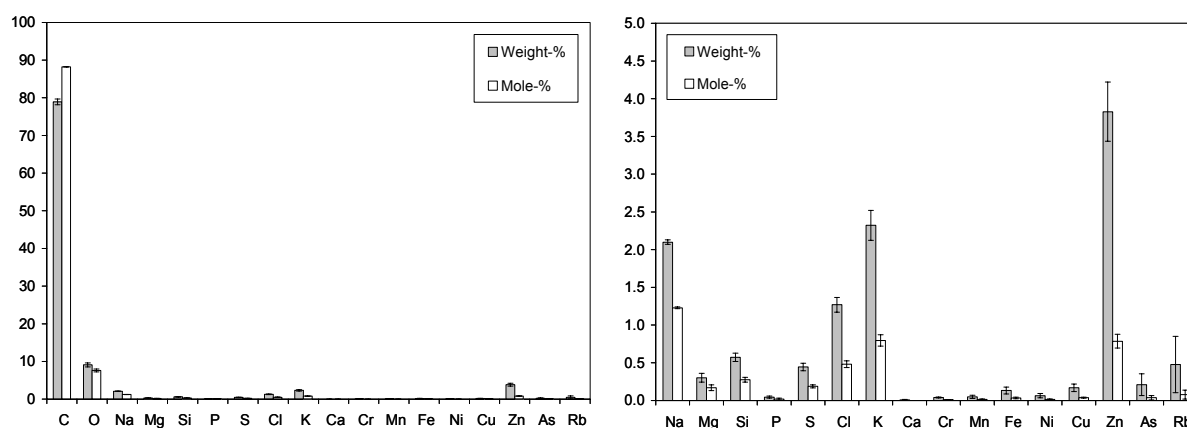


Figure 19.a) Elemental composition of fine mode particles in the emissions from birch wood combustion in the wood stove (mode 1, exp 2, intermediate phase). Results presented as average values of 3 area analyses (100*100 μm) on impactor stage 3 (D_g=130 nm) with standard deviation shown as error bars. In the left diagram all analyzed elements are shown, and in b) different scaling is used to get a better resolution of the less abundant elements (C and O not shown). Aluminum was excluded from the analysis since Al-foils were used as sampling substrates.

The amount of carbonaceous material was relatively low in the PM from the pellet stove combustion and in Figure 20, the relative elemental composition of inorganic elements in the fine particles from the pellet stove experiments are shown on a carbon and oxygen free basis. In accordance with previous data from residential pellet burners (*Paper III*), the fine inorganic PM was dominated by potassium, sulfur and chlorine in the form of K_2SO_4 , $K_3Na(SO_4)_2$ and KCl . Sodium and in some cases also zinc were also found as important elements in the fine PM. Alkali carbonates were not detected in the analysis but could not be excluded as additional alkali phases in some cases. The degree of volatilization, subsequent gas-to-particle conversion and final phase composition may, however, differ significantly since it influenced by combustion temperature, local air to fuel ratio and fuel properties/composition.

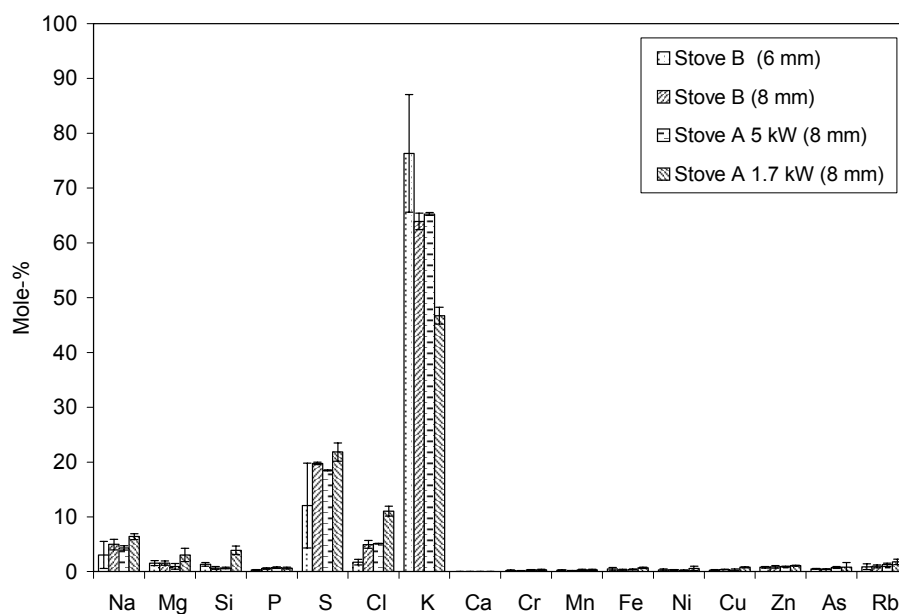


Figure 20. Relative elemental composition (on a C, O and Al free basis) for the fine mode particles in the emission from combustion of softwood pellets in two pellet stoves. Results presented as average values of 3 area analyses ($100 \times 100 \mu m$) on impactor stage 3 ($D_g=130 \text{ nm}$) with standard deviation shown as error bars.

Figure 21 shows a micrograph of fine particles sampled on impactor stage 3 ($D_g=130 \text{ nm}$) during high load combustion in a pellet stove. The PM seems to consist of spherical particles in the range of 100 nm more or less agglomerated in larger structures which may a sampling effects or the presence of (partly) melted salt particles in the flue gases. A possible effect on particle morphology from the potential water up-take of hygroscopic alkali salts also exists.

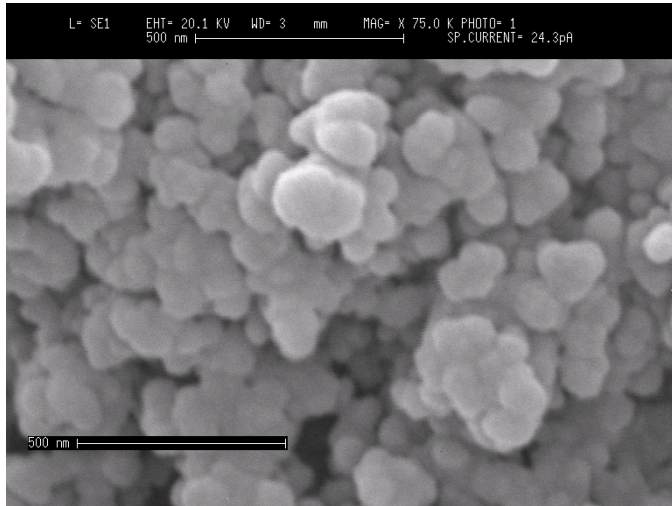


Figure 21. SEM image of a bulk sample of fine mode particles on impactor stage 3 ($D_g=130$ nm) sampled in the emissions from pellet stove B during high load combustion.

Based on the extensive characterization and quantification work within the project with residential wood log and pellet stoves, as discussed above, emission factors and their variability can be extracted. As discussed previously, significant higher emissions, mainly of PIC's, were generally determined during wood log combustion than pellets combustion. However, significant variations in emission factors were also determined for specific appliances as a function of variations in combustion conditions, fuel properties and operation.

In Figure 22, the average emissions of the main components determined during the different campaigns are presented. To illustrate the emission levels and their variations determined for the pellet stoves, the emissions factors determined at different fuel loads are presented in Figure 23.

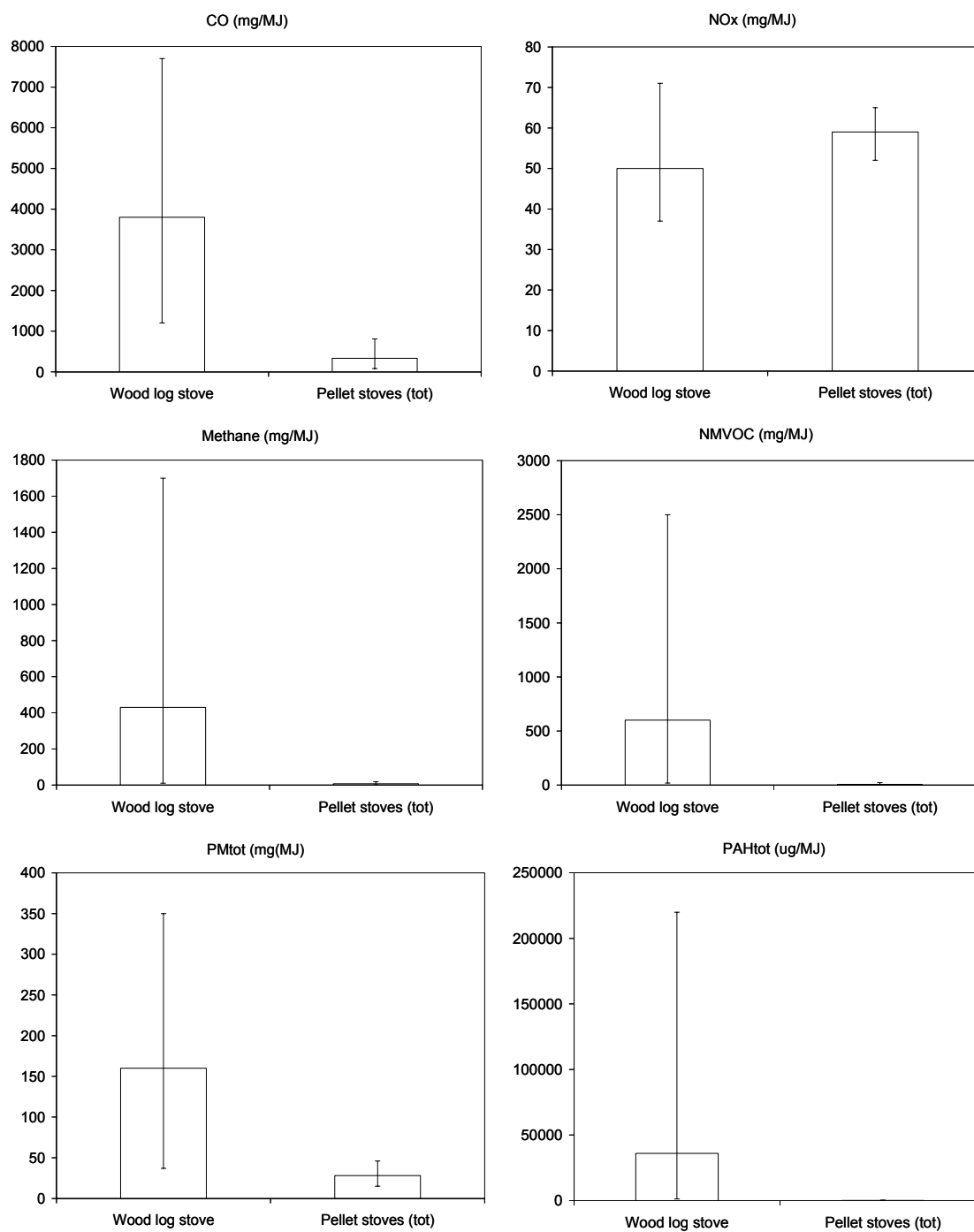


Figure 22. Summary of average emission factors of the main components determined for the wood log and pellet stoves, with the interval shown for highest and lowest average values determined during different experiments in the present campaigns.

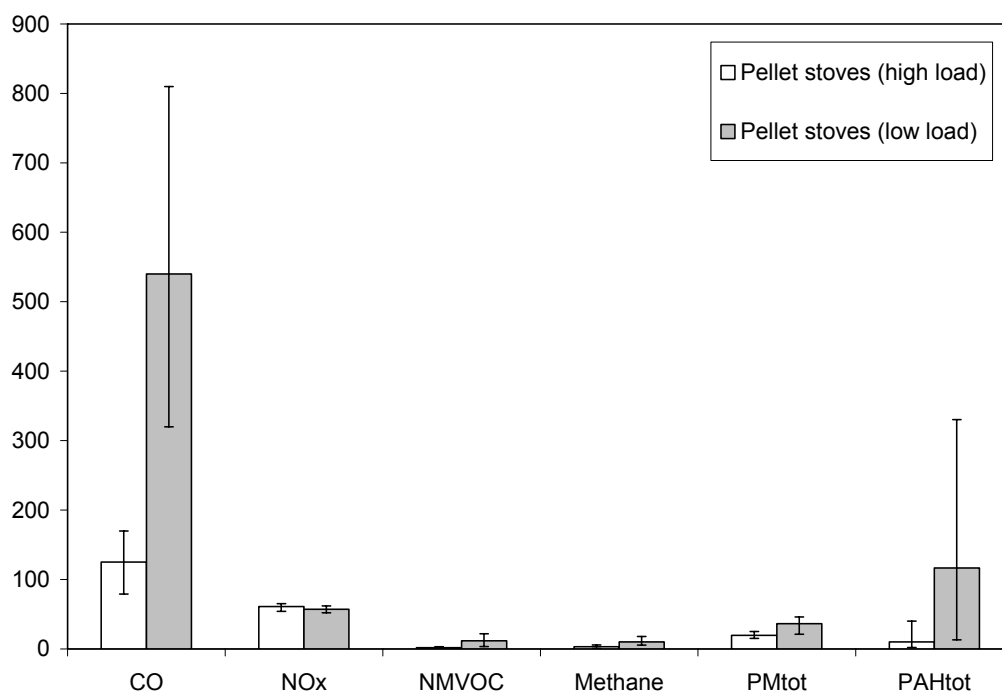


Figure 23. Summary of average emission factors for the pellet stoves during high (5-6 kW_{fuel}) and low (2 kW_{fuel}) load operation, with the interval shown for highest and lowest average values determined during different experiments in the present campaigns.

3.6 Effects of temperature and residence time on the emissions (Paper VI)

As shown in our previous work on residential biomass stoves (**Paper V**) as well as by others for boilers [76], the use of fuel pellets provides possibilities for considerable reduced emissions of PIC's compared to residential wood log combustion. Traditionally, residential wood log appliances often suffer from incomplete combustion conditions caused by air starving, temperature in-homogeneities and/or short residence times at sufficiently high temperatures, resulting in excessive amounts of PIC's. Although the impact of conversion from wood log to pellet combustion is considerable, the need for further reduction in emission levels for pellet appliances to facilitate a significant conversion from oil and electricity heating to residential biomass combustion with preserved air quality has been emphasized [87]. Recent results have also shown that the waste amounts of simple gaseous PIC's (e.g. CO and gaseous hydrocarbons) relatively easily can be avoided by isothermal, high temperature combustion of biomass pellets [88]. However, no similar data is available for PAH and PM. Formation and destruction of tars and PAH have recently been reviewed and many compounds are generally considered to need high temperature and reaction severities for thermal destruction [89, 90]. Actual controlled studies of the effects of combustion temperature, isothermal conditions and residence times in the post-combustion zone during firing of pelletized softwood fuels have not yet been reported.

The effects of temperature and residence time in a laboratory fixed-bed pellets reactor (Figure 24) on the emission formation/destruction and characteristics of PIC's, especially

PAH, and PM was therefore determined. Temperature and residence time after the bed section in the reactor was varied according to statistical experimental design covering the ranges 650-970°C and 0.5-3.5 s, respectively. Also in this study, typical softwood pellets were combusted at 2 kW_{fuel}, corresponding to a typical situation for small houses during wintertime. The previously designed and evaluated dilution sampling setup was used and the emission responses were; CO, organic gaseous carbon (OGC), NO, VOC including 20 specific compounds, PAH (particulate + semi-volatile PAH) including 43 specific compounds, PM_{tot}, particle mass and count median diameter (MMD and CMD) and particle number concentration.

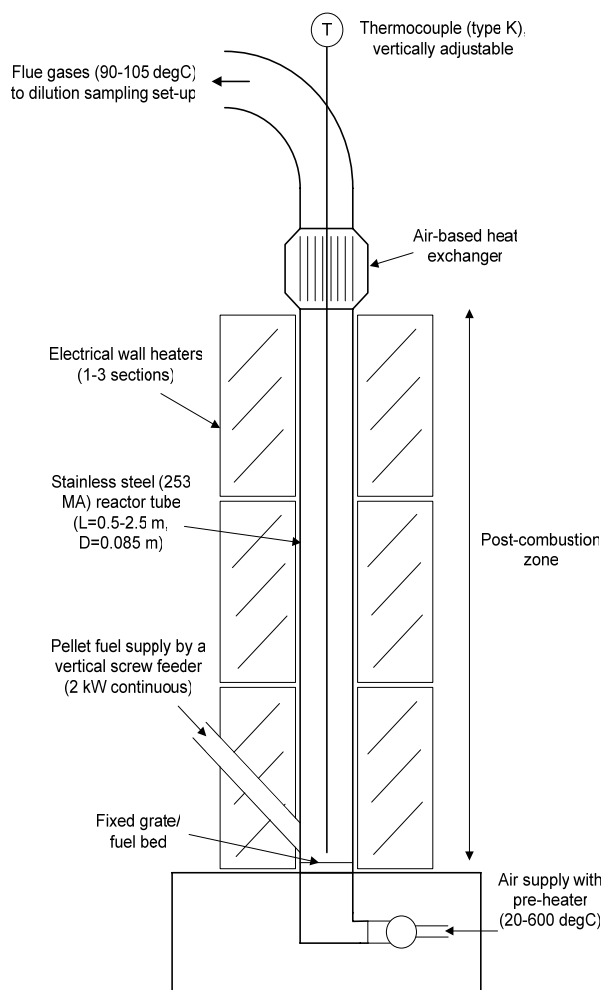


Figure 24. Schematic illustration of the experimental fixed-bed pellets reactor (<5 kW_{fuel}).

Temperature was negatively correlated with the emissions of all studied PIC's, i.e. higher temperature resulted in lower PIC emissions with no significant effect of residence time. As seen in Figure 25, the concentrations of all studied PAH's were decreased drastically with almost a total depletion at temperatures above 850°C. For NO, a reversed correlation with temperature was determined, i.e. increasing emissions with increasing temperature. The PM_{tot} emissions were in the range of 15-20 mg/MJ with no effect of variations in temperature or time determined. The PM was totally dominated by fine (<1 µm) particles consisting of potassium, oxygen, sulfur, carbon, chlorine, sodium and zinc. Fine particle mass and count

median diameters as well as number concentration were significantly influenced of residence time, i.e. increased time resulted in increased particle sizes and decreased number concentrations. The mass and count median diameters varied in the range of 100-180 nm and 80-105 nm respectively, with number concentrations in the range of $3-7 \cdot 10^{13}/\text{MJ}$.

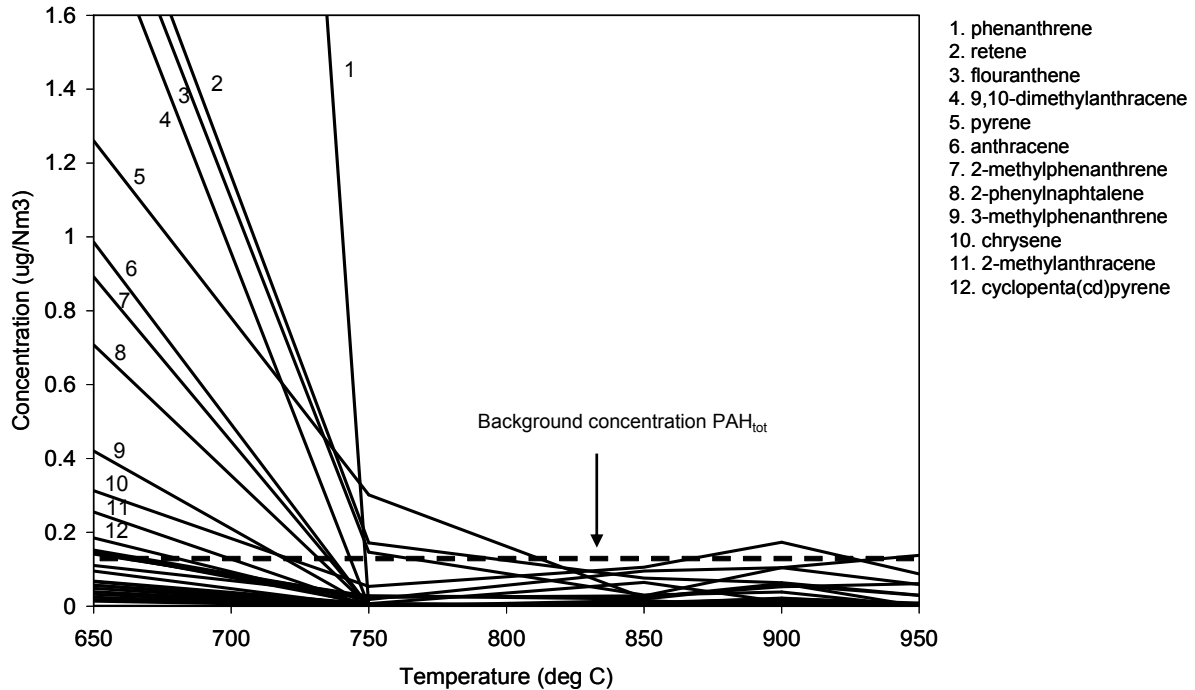


Figure 25. Concentrations of separate PAH compounds in the flue gases during combustion of softwood pellets as a function of temperature in the post-combustion zone after the fuel bed.

The results in the present study showed that it exist a significant potential to obtain optimized combustion conditions in residential pellet appliances with in principal a total depletion of PIC's by high temperature, intensive, air rich and well mixed conditions in the bed section. During such conditions, the importance of residence time at high temperature was shown to be limited although isothermal conditions during 0.5-1.0 s would be preferable for optimized results in practical situations. Such high temperature conditions in the fuel bed, which resembles the conditions in present commercial pellet appliances, may however, increase the risk for potential ash related problems like slagging, especially during combustion of some qualities of more ash rich pellet fuels as discussed in **Paper IV**. If such fuels are to be used and potential ash related problems should be prevented, air staging with lower fuel bed temperatures is preferable and the importance of sufficiently long residence time in the post-combustion zone for minimizing the emissions of PIC's will therefore increase. The extremely low emissions of PAH and other PIC's can probably be explained by a prevention of the formation or instant oxidation rather than thermal destruction in the post-combustion zone. Although these results and conclusions are exciting and encouraging they may be consequences of both the excess surface temperatures of the burning fuel pellets and more reactor specific conditions, emphasizing the need for further verification studies and technology development work.

3.7 Trace element enrichment and behaviour during wood pellet production and combustion (Paper VII)

The concerns regarding environmental dispersion of toxic heavy metals (e.g Cd, Pb and Hg) are extensive and well documented and constitute solid motives for the special focus of the fate and forms of these elements in different processes. The presence of different particle associated transition metals (e.g. Cu, Zn, V and Ni) have also been suggested to be one of several properties that may elucidated the link between different observed adverse health effects and exposure to particulate matter (PM) in the ambient air [71, 72, 91]. The use of direct exhaust gas drying with combustion flue gases is today a commonly used method in fuel pellet production and previous findings gave rise to the question whereas a potential contamination also of trace elements may exist during the pellets production process. Since many of the trace elements present in biomass are potentially volatile at combustion conditions [92], an understanding of their presence and behavior is of fundamental importance for controlling and minimizing the environmental dispersion.

The potential enrichment of trace elements during the production process, i.e. drying procedure of the raw material, as well as their behaviour during combustion in different applications was therefore studied in a combined field sampling and chemical equilibrium modeling work. Extensive sampling and analysis of the raw material and produced pellet fuel was performed at two different pelletizing plants in Sweden (northern and southern) to evaluate the potential effects of the use of direct drying gases from biomass (bark) combustion. Sampling of particulate material by PM_{tot} and DLPI was also performed in the drying gases. In addition, chemical equilibrium model calculations were performed using the software program FACTSage 5.2 for typical softwood sawdust and bark fuels with variations in the content of trace elements, moisture, sulfur and chlorine both at global oxidizing conditions as well as local reducing atmospheres.

A significant enrichment of the volatile trace elements Zn, Cu, Cd and Pb was documented from the field sampling campaign in the plant using bark combustion gases for drying of the sawdust (Figure 26), and also supported by chemical equilibrium results. This is caused by the volatilization of these elements from the bark fuel during combustion with subsequent formation of fine particles in the flue gases and finally captured in the pellet raw material. In both plants, also a trend of enrichment of Cr and Ni in the pellets was determined. However, the presence and magnitude of the increased concentrations varied considerably between different samples, presumably explained by mechanical wearing and captivation of super micron particles or dust from stainless steel components.

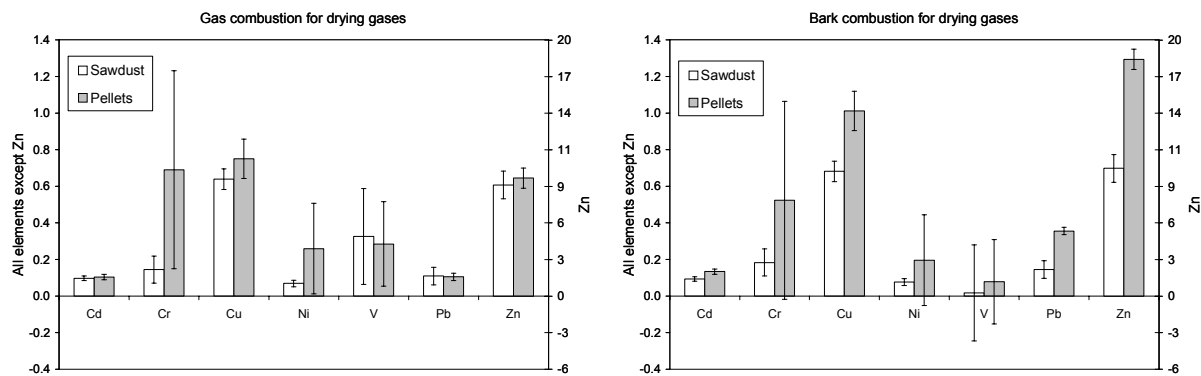


Figure 26. Concentrations (mg/kg d.wt.) of trace elements in the raw material (saw dust) and produced fuel pellets in the northern (left, 11 samples) and southern (right, 10 samples) pellet production plant, with standard deviations shown as error bars.

Although a significant enrichment of Zn, Cu, Cd and Pb were determined, when bark combustion gases were used in the drying process, the contents determined in the produced pellet fuels were overall found to be in same range as previously reported average data for different biofuels, including wood pellets and bark. They were all also well below typical metal concentrations in municipal solid waste (Cd 3.5 mg/kg, Pb 1200 mg/kg, Zn 1200 mg/kg). Based on both experimental particle sampling and chemical equilibrium predictions, a potentially high volatility of the trace elements of concern (Zn, Cd and Pb) can be assumed during combustion both for softwood sawdust (pellets) and bark (drying fuel). Cd and Pb was predicted to be fully volatilized under all studied conditions. Zn, however, is fully volatilized in reducing conditions within burning fuel particles, but requires over 1100-1150°C to be volatilized at global oxidizing conditions. For Cu, the volatilization is highly influenced mainly by the chlorine available during oxidizing global conditions, forming gaseous CuCl_2 in the range of 700-1050°C. For the bark fuel in general as well as for wood under reducing conditions, the volatilization temperature was predicted between 950°C and 1100°C with only limited effects of the variations studied.

An estimation of the national emissions from heating in the residential sector reveals that the increased amount emitted by the potential enrichment in pellets corresponds to 45% for Zn, 3% for Cu, 5% for Cd and 2% for Pb. The significant relative increase in estimated emissions of Zn from the residential sector is probably also caused by an underestimation of the volatility and thereby emission of zinc from small scale biomass combustion in the national air pollution inventory data [93]. It is also important to consider the relative importance for different applications for the total mass fluxes and emissions of different trace elements. In contrast to residential appliances, large and medium sized biomass boilers are for example usually equipped with some kind of efficient particle separation system, either electrostatic precipitator or fabric filters. In conclusion, a potential enrichment of trace elements like Zn, Cu, Cd and Pb in wood fuel pellet production processes exists when (un-cleaned) combustion gases from trace element rich fuels, e.g. bark, is used for production of drying gases. The magnitude and relative importance of such enrichment seems, however, to be rather small in comparison to typical concentrations in similar and other types of biomass fuels. In addition, some alternative measures for prevention of trace metal contamination during fuel pellet production were suggested, including fuel quality aspects, high temperature particle separation and in-direct drying processes.

4 CONCLUSIONS

Based on the results obtained in the thesis, the following general conclusions with implications for the understanding of the formation and characteristics of particulate and gaseous emissions from residential biomass combustion, future environmental health impact assessments, legislations and technical development of residential biomass combustion systems can be draw:

Emissions from residential biomass combustion include a number of air pollutants with potential adverse health effects, and an increasing interest concerning their potential implications to human health can be seen. A limited number of dedicated epidemiological studies have been performed but substantial quantitative information is found for acute asthma in relation to PM₁₀. Ambient exposure to combustion related fine particles in general have also been associated with cardiopulmonary disease and mortality as well as cancer risks, but the importance of other particulate properties than mass concentration, like chemical composition, particle size and number concentration remain to be elucidated.

The methodology and conditions during sampling of emissions from small combustion appliances can significantly influence the emission characteristics, especially concerning the (semi-volatile) organic fraction of the aerosol. A set-up for whole flow dilution of the flue gases was evaluated and proven to be a suitable method to characterize the emissions under controlled and more ambient-near conditions.

Extensive quantification and characterization of particulate and gases emissions was performed for a wide range of residential biomass combustion appliances during different fuel and operational conditions. Emission factor ranges for wood and pellet stoves were determined and a significant variability of emission performance during different conditions was found with considerable emissions of PIC's (e.g. CO, hydrocarbons and soot) obtained during specific situations, especially for batch wise wood log combustion. However, the emissions of PIC's can be rather well controlled by proper technical and/or operational measures, and a significant potential for further development and optimization therefore exists.

VOC and PAH emission characteristics were determined for a wide range of residential biomass combustion appliances during different fuel and operational conditions. Beside methane, major VOC's were ethene, acetylene and benzene with NMVOC emissions in the range 20-2500 mg/MJ for wood stoves and 1-20 mg/MJ for pellet stoves. PAH_{tot} emissions were determined in the range of 1300-220000 µg/MJ for wood stoves and 2-300 µg/MJ for pellet stoves with phenantrene, fluoranthene and pyrene generally in all cases found as major PAH's. Retene was also found in considerable concentrations only during combustion of conifer wood logs, in similar ranges for pine and spruce, as well as during somewhat poorer combustion of softwood pellets.

In all cases, the emissions of PIC's as well as PM_{tot} were shown to be considerably higher from wood stoves compared to those from pellet stoves. Accordingly, the use of up-graded pellets biomass fuels, combusted under continuous and controlled conditions give advantageous combustion conditions compared to traditional batch wise firing of wood logs. There is, however, still a significant potential for further minimization of PIC emissions in future pellets technology, especially at low load operation.

The total emissions of particulate matter (PM_{tot}) varied in the range of 35-350 mg/MJ_{fuel} for wood log stoves and 15-45 mg/MJ_{fuel} for the pellet stoves. Fine (<1 μm) particles in the range of 100-300 nm (MMD) dominated in all cases the PM with 80-95% as PM_1 . CMD and number concentrations of the fine particles varied in the range of 50-250 nm and $4.6 \cdot 10^{12}$ - $1.1 \cdot 10^{14}$ particles/MJ, respectively. Mass concentrations and size distributions of fine particles were clearly influenced by combustion conditions as an effect of increased formation of soot and organic material during poorer conditions.

The minor and varying coarse (>1 μm) fraction sometimes present consisted either of entrained mineral particles (e.g. CaO/CaCO₃ and silicates) or as carbonaceous unburned fuels residues, with inclusions (1-10 μm) of calcium containing grains.

These variations in PM emissions and size distributions were caused by variations in combustion conditions when using different fuels, appliances and operating procedures. The influence on PIC's (i.e. soot and organic material) on the aerosol characteristics was clearly illustrated. During optimized combustion of softwood pellets, the PM is totally dominated by inorganic particles with emission factors of 15-20 mg/MJ_{fuel}. Potassium, sulfur and chlorine dominated generally the fine inorganic PM emissions in the form of K₂SO₄, K₃Na(SO₄)₂ and KCl, although some variations were determined. The pronounced presence of K₃Na(SO₄)₂ is of general importance concerning possible formation and transformation mechanism of fine alkali particles. Besides the alkali metals (K and Na), zinc was found as an important elements in fine particles from residential biomass combustion, presently found in a more complex form other than pure ZnO or any simple zinc salt. During combustion, almost all zinc may be volatilized as Zn (g) within the reducing atmospheres of the burning fuel particles, subsequently at lower temperatures captured in the fine particle fraction. However, the formation mechanism and exact phase composition of the zinc containing phase(s) remain to be determined.

The importance of high temperature (>850°C) in the bed zone with intensive, air rich and well mixed conditions with isothermal conditions for 0.5-1.0 s in the post combustion zone was illustrated for wood pellets to obtain complete combustion conditions with almost a total depletion of PIC's. Considering the use of modern and "low-emitting" residential biomass combustion technologies using different biomass fuels and their potential implications for air quality and human health, some of the most urgent questions at issue seem to be to determine the formation mechanisms, detailed chemical characteristics and potential environmental health effects for the alkali and trace element (e.g. zinc) containing fine particles.

The present work further clearly illustrated the benefits of combining dedicated experimental work with careful chemical equilibrium calculations under different local conditions for a mechanistic understanding of the ash transformation processes.

The ash formation and transformation processes during combustion in residential appliances is of vital importance both for the performance and accessibility of the system as well as for the potential capture and/or release of aerosol forming elements of concern, e.g. alkali and specific trace elements. The use of other raw materials (or contaminated stem-wood) then pure stem-wood assortments may significantly influence the potential alkali silicate formation, i.e. induce alkali retention and potential ash related problems, as well as amount and forms of alkali and trace elements containing fine particles.

The behaviour of different trace elements relevant for biomass fuels during pellets production and use (combustion) were studied by field sampling of fuels and particulates as well as chemical equilibrium calculations. A significant enrichment of some trace elements in pellet fuels was found as a result of the production/drying process. Volatile elements like Zn, Cu, Cd and Pb were somewhat enriched from the use of bark as drying fuel. The magnitude and importance of such enrichment is, however, relatively small compared to typical concentrations in wood and bark fuels as well as compared to present estimations of the national emissions of these elements.

5 PROSPECTS OF FUTURE WORK

The closely linked research fields of combustion related energy production, air pollution and environmental health calls for:

- a solid basic understanding of the processes and mechanisms that control the behaviour of different pollution by-products during combustion, dispersion and exposure
- multidisciplinary joint collaborations within fields of e.g. combustion engineering, process chemistry, aerosol science, atmospheric science and respiratory and cardiovascular medicine.

Large number of interesting questions of issue arisen from the work within or related to this thesis can therefore be identified as highly relevant and urgent tasks for future work, of which some already have been concretized and initiated.

In a project financed by the Swedish National Air Pollution Programme (SNAP, S-EPA) dedicated human exposure studies with different biomass related pollutants and mixtures will be performed. The project is an inter-disciplinary collaboration between *Energy Technology and Thermal Process Chemistry at Umeå University* and three other research groups: *Nuclear Physics* (Prof Erik Swietlicki, MSc Jakob Löndahl et al) and *Ergonomics and Aerosol Technology* (Prof Mats Bohgard, Dr Joakim Pagels et al) at *Lund Institute of Technology* and *Respiratory Medicine & Allergy* (Prof Thomas Sandström, MD PhD Anders Blomberg et al) at *Umeå University Hospital*. The project, that has considerable potentials, initially comprises: i) detailed characterization of biomass combustion aerosols generated under different conditions, ii) controlled generation of synthetically produced (combustion) aerosols, iii) determination of biological responses during controlled chamber exposures and iv) determination of respiratory particle deposition.

Future work more related to combustion process chemistry, fuel quality and emission characterization and may involve:

- detailed determination of the mechanisms that govern the ash transformation processes during combustion of present and potentially new raw materials, with focus on alkali and trace metal aerosol formation and characteristics, by studying the chemical processes in actual and synthetic combustion atmospheres and combining different sampling and analysis methods, e.g. molecular beam mass spectrometry (MBMS), high temperature particle sampling, in-situ aerosol measurements, XRD, XAFS, SEM and TEM (transmission electron microscopy).
- determine the potentials to influence the ash transformation processes, reduce the fine ash particle formation, capture trace elements and control the chemical composition by adding different reactive or sorbent materials, either during fuel production or by injection during combustion.
- studies of the fate and forms of the organic fraction of the aerosols during biomass combustion concerning particle gas phase partitioning, chemical composition and potential health effects compared to traffic related emissions.
- further evaluate and validate the possibilities for emission (PIC) minimization, also for commercial residential biomass wood log pellet appliances, especially at varying and low-load operation.

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Å hur går det
här då ?

Öhh ... inte
riktigt klar
än ...!

