Ash formation in circulating fluidised bed combustion of coal and solid biomass

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Abstract

Formation mechanisms of the fly ash and bottom ash during circulating fluidised bed combustion of a bituminous coal and two solid biomass fuels were studied experimentally. The biomass fuels were forest residue and willow (Salix). The experiments were carried out at full-scale boilers. As a result, the main ash formation mechanisms are presented for coal and biomass combustion.

Ash formation was studied using the methods of traditional ash sampling and aerosol technology. By traditional ash sampling methods, samples of ash were collected from different ash streams of the boiler. The collection streams were the fuel feed, sorbent or bed material feed, boiler bottom ash, and the fly ash collected in the electrostatic precipitator. The methods of aerosol technology enabled sampling of the particles directly from the flue gas flows. In this way, the size distributions of the particles were determined. In addition, the elemental contents of the particles were analysed with different methods to obtain the concentrations of the different ash compounds in the flue gas. The aerosol instrumentation included the following devices: low-pressure impactors, cyclones, a differential mobility analyser combined with a condensation nucleus counter and an electrical low-pressure impactor. The morphology of the particles was analysed using scanning electron microscopy.

In coal combustion, limestone sorbent was used to capture SO_2 and no additional bed material was utilised. The bottom ash consisted mainly of coal minerals and unfragmented sorbent particles. The coal minerals agglomerated during combustion forming bottom ash particles with a wide range of compositions. Sorbent particles captured SO_2 and were mainly present as $CaSO_4$ and CaO. During biomass combustion, quartz sand was fed into the furnace to maintain an adequate bed inventory. No sorbent was used. The adhesion of ash to the sand particles and the subsequent growth of bed particles formed the

bottom ash. The ash compounds adhered to the sand particles by two mechanisms: i) adhesion of the non-volatile ash compounds as particles on the sand surface, and ii) diffusion of the volatile ash compounds into the quartz sand and subsequent chemical reaction. The ash particles formed a sticky layer on the sand particles which in high temperatures or when grown sufficiently thick might have caused agglomeration and deposition problems in the bed as well as in the upper parts of the furnace and in the cyclone loop.

The fly ash size distributions were bimodal with all fuels. The fine mode was formed in the submicron size range by volatilisation and subsequent nucleation of the volatilised species. These particles then grew by condensation. The mass of the fine particle mode consisted 0.3 % of the total mass of the fly ash particles during coal combustion, 2 % during forest residue combustion, and 8 % during willow combustion. The major fraction of the mass in the fine mode consisted of HCl with coal, KCl with forest residue, and K_2SO_4 with willow. The coarse fly ash particles, so-called residual ash, were formed mainly from the ash compounds that did not volatilise during combustion. The coal minerals formed agglomerates with a few minerals in one particle. In addition, a major proportion of the limestone sorbent fragmented and escaped the furnace as fly ash. The coarse fly ash particles from biomass combustion were large agglomerates comprised of mainly submicron-sized primary particles up to several thousand in number.

The agglomerate shape of the particles was found to affect the gas-to-particle conversion of the volatilised species. Consequently, the resulting concentration size distributions were different from those for spherical particles. Condensation of the volatilised species resulted in the enrichment of the condensed species in the fine particles whereas the gas-to-particle conversion by a chemical surface reaction resulted in a concentration of the volatilised species that did not depend on the particle size.

Preface

This thesis work was carried out at the Aerosol Technology Group of VTT Chemical Technology. I want to thank all my colleagues in the group for a great working atmosphere. Especially, I wish to express my gratitude to the head of the group, Dr. Esko I. Kauppinen, for guiding me through the first steps in my research. When I first started my research work, his relentless enthusiasm towards scientific work was quite captivating – it was a great inspiration for this thesis. I am deeply indebted to professor Rainer Salomaa from the Laboratory of Advanced Energy Technologies of Helsinki University of Technology for encouragement and supervision.

I dedicate my warmest thanks to Dr. Martti Aho and Dr. Jorma Keskinen for helpful comments – they certainly made the thesis better. Thanks for comments are also due to Dr. Bertram Schleicher, and for linguistic revision for Mr. Ronald Dwight.

I want to extend my gratitude to all my co-authors and the researchers involved in the work. Mr. Tuomas Valmari was invaluable in the biomass studies and I sincerely thank him for the productive co-operation. Dr. Jorma K. Jokiniemi is acknowledged for many fruitful discussions. I want to thank Mr. Juha Kurkela not only for his contribution in the result analysis and the experimental work, but also for sharing the office room with me for several years, and for all the discussions, mostly highly unrelated to research. I also thank the analysts professor Willy Maenhaut, professor Frank E. Huggins, Dr. Anup Shah, and Dr. Tuomo Pakkanen for participation in this work. I am grateful to Ms. Kristina Nilsson, Dr. George Sfiris, and Mr. Raoul Järvinen for the work carried out during the experiments.

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Contents

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Publications

A   Lind, Terttaliisa; Kauppinen, Esko I.; Maenhaut, Willy; Shah, Anup and Huggins, Frank. (1996) Ash Vaporization in Circulating Fluidized Bed Coal Combustion. *Aerosol Sci. Techn.*, Vol. 24, No. 3, pp. 135–150.

B   Lind, Terttaliisa; Kauppinen, Esko I.; Kurkela, Juha; Maenhaut, Willy; Shah, Anup and Huggins, Frank. (1995) Mineral, Sorbent and Sulfur Interactions in Real-Scale CFBC. *Proceedings of the 13th International Conference in Fluidized Bed Combustion. Heinschel, Kay J. (Ed.).* ASME. Pp. 1129–1136.

C   Lind, Terttaliisa; Kauppinen, Esko I.; Jokiniemi, Jorma K.; Maenhaut, Willy and Pakkanen, Tuomo A. (1994) Alkali Metal Behaviour in Atmospheric Circulating Fluidised Bed Coal Combustion. In: *The Impact of Ash Deposition on Coal Fired Plants*. Williamson, J. and Wigley, F. (Eds.). Taylor & Francis. Pp. 77–88.

D   Lind, Terttaliisa; Kauppinen, Esko I.; Jokiniemi, Jorma K. and Maenhaut, Willy. (1994) A Field Study on the Trace Metal Behaviour in Atmospheric Circulating Fluidized-Bed Coal Combustion. *Twenty-Fifth Symposium (International) on Combustion*. The Combustion Institute, Pittsburgh, PA. Pp. 201–209.

E   Lind, Terttaliisa; Kauppinen, Esko I.; Sfiris, George; Nilsson, Kristina and Maenhaut, Willy. (1998) Fly Ash Deposition onto the Convective Heat Exchangers during Combustion of Willow in a Circulating Fluidized Bed Boiler. Accepted for publication in *The Impact of Mineral Impurities in Solid Fuel Combustion*. Proceedings of the Engineering Foundation Conference, Kona, HI, November 2–7, 1997. 14 p.

F   Lind, Terttaliisa; Valmari, Tuomas; Kauppinen, Esko I.; Sfiris, George; Nilsson, Kristina and Maenhaut, Willy. (1999) Volatilization of the Heavy Metals during Circulating Fluidized Bed Combustion of Forest Residue. *Environ. Sci. Techn.*, Vol. 33, No. 3, pp. 496–502.

G   Valmari, Tuomas; Lind, Terttaliisa M.; Kauppinen, Esko I.; Sfiris, George, Nilsson, Kristina and Maenhaut, Willy. (1999) Field Study on Ash Behavior during Circulating Fluidized-Bed Combustion of Biomass. 1. Ash Formation. Accepted for publication in *Energy & Fuels*.

H   Valmari, Tuomas; Lind, Terttaliisa M.; Kauppinen, Esko I.; Sfiris, George; Nilsson, Kristina and Maenhaut, Willy. (1999) Field Study on Ash Behavior during Circulating Fluidized Bed Combustion of Biomass. 2. Ash Deposition and Alkali Vapor Condensation. Accepted for publication in *Energy & Fuels*.

Author's contribution

This thesis work was carried out at the Aerosol Technology Group of VTT Chemical Technology during 1990–1998. Papers A–D present results from coal combustion. The author of the thesis carried out the experimental work in cooperation with and under the supervision of Dr. Esko I. Kauppinen. In addition, she conducted the data analysis, interpreted the results and wrote the publications. Co-authors of the publications carried out elemental and CCSEM analysis of the samples. In paper C, Dr. Jorma K. Jokiniemi carried out the aerosol model calculations and the interpretation of the modelling results. In paper B, Mr. Juha Kurkela carried out the data analysis of the CCSEM results.

Papers E–H describe the ash transformations during biomass combustion. Dr. Esko I. Kauppinen supervised the work. The author of this thesis carried out the experimental work during combustion of willow. The experiments during combustion of forest residue were carried out together with Mr. Tuomas Valmari. The author conducted the data analysis and writing of the papers E and F, and interpretation of the results for paper E. The results for papers F–H were interpreted in cooperation with Mr. Tuomas Valmari who carried out the data analysis and writing of the papers G–H. Dr. George Sfiris and Ms. Kristina Nilsson took part in the experiments and Dr. Willy Maenhaut carried out the elemental analysis of the samples.

List of symbols and acronyms

A	constant in the agglomerate power law
A_1	Area of a primary particle
A_{aggl}	Area of an agglomerate
A_{eff}	Effective area of a spherical particle
D_1	Diameter of a primary particle
D_{aggl}	Mobility diameter of an agglomerate
D_p	Particle diameter
D_v	Diffusion coefficient
I	Net rate of arrival of the vapour molecules
k	Boltzman number
m_i	Mass of the element i
m_{tot}	Total mass of a particle
m_v	Mass of a vapour molecule
N	Number of primary particles in an agglomerate
p	Partial pressure of a vapour in the gas
p_d	Saturation vapour pressure, takes into account Kelvin effect
p_s	Saturation vapour pressure
R_f	Fractal dimension
T	Temperature
V_1	Volume of a primary particle
V_{aggl}	Volume of an agglomerate
V_p	Volume of a spherical particle
λ	Gas mean free path

btoe	billion tons of oil equivalent
CCSEM	Computer controlled scanning electron microscopy
CFB	Circulating fluidised bed combustion
CNC	Condensation nucleus counter
DMA	Differential mobility analyser
ELPI	Electrical low-pressure impactor
ESP	Electrostatic precipitator
LPI	Low-pressure impactor
MSW	Municipal solid waste
SEM	Scanning electron microscopy

1. Introduction

Fossil fuel combustion is a major energy source in the world. Fossil fuels have been used for energy production for several centuries, and their combustion has been a strong driving force behind the industrial revolution since the late 18th century. Lately, the rapidly growing use of fossil fuels has been causing severe environmental impacts due to pollutant emissions. Acid rain is caused by the emissions of nitrogen and sulphur oxides (NO_x, SO_x) which convert to nitric and sulphuric acid in the atmosphere. Particle emissions, especially fine particles, have been found to be a health risk (Pope et al., 1995). In addition, carbon dioxide (CO_2) emissions have increased the CO_2 concentration in the atmosphere. This is expected to increase the greenhouse effect and hence the average temperature on earth.

The consequences of fossil fuel combustion have been realised and the industrial countries have taken rather strict actions to reduce the emissions of nitrogen and sulphur oxides as well as those of particles. These actions have been beneficial for the environment as the nitric and sulphuric acid fall-outs have clearly been decreased during the past decade. Also, particle emissions have been reduced significantly. However, CO_2 emissions are harder to reduce. The amount of CO_2 that is generated during combustion is so large that its post-combustion reduction becomes expensive. Its storage has also been investigated but the needed storage space is huge. Therefore, other means to reduce CO_2 emissions into the atmosphere are sought continuously. There are two ways to reduce the CO_2 emissions from combustion processes: i) to make the processes more efficient, i.e. produce more energy for a certain amount of CO_2, or ii) to use fuels which are neutral in regard to CO_2.

One of the means to reduce CO_2 emissions is to make the combustion processes more efficient. Higher efficiency means that while burning the same amount of fuel, more electricity and heat is produced. Hence less CO_2 is produced for a given amount of electricity and heat. Coal utilisation processes that are more efficient than the conventional combustion processes are for example co-generation of electricity and heat, and advanced coal conversion processes. These advanced conversion processes include pyrolysis, gasification and combustion processes as well as different combinations of the three. One of the technologies used for more efficient conversion processes is fluidised bed

reactor which has many advantages compared to the conventional pulverised fuel and grate-fired boilers. While the electricity production efficiency of the conventional coal combustion processes is presently approximately 30–45%, efficiencies up to 55% have been estimated to be possible with advanced coal conversion processes. Using natural gas, electricity generation efficiencies up to 60% can be achieved.

Another means to reduce CO_2 emissions from combustion is the use of alternative, CO_2 neutral fuels. All organic fuels produce CO_2 as a combustion product, but biomass fuels – trees and other plants – can be regarded as CO_2 neutral because they consume the same amount of CO_2 for their growth as is released during their combustion. Therefore, within the plants' growth-combustion cycle, they use as much CO_2 for growth as they emit in combustion. The length of the growth-combustion cycle depends on the growth rate of the plants and varies greatly between different biomass fuels. It can be as short as a year for fast-growing, short-rotation crops, but it can take up to 100 years for large trees. This means that all biomass can be regarded as CO_2 neutral if a period of at least 100 years is considered.

Mankind has a long tradition of using biomass for energy production. A wide variety of biomass fuels are used in the world, depending on the country and its resources: wood-based fuels, agricultural wastes such as straw, rice husk, bagasse, grass, and many others. By far, the most widespread use of biomass is in the small fireplaces for cooking and heating in the developing countries. Annual biofuel consumption in developing countries is over one billion tons of oil equivalent (btoe). That is three times the consumption of coal in Europe (0.28 btoe), and double the consumption of coal in the USA (0.47 btoe) (Barnes and Floor, 1996). In the developing countries, two billion people are still dependent on biofuels for cooking.

Large scale biomass combustion facilities have also been constructed, and with the urgent need for CO_2 emission reductions, more facilities are being built all over the world (van den Broek et al., 1996). For instance, The European Union has set a goal to increase the use of biomass for energy production with 200% by year 2010, the Asian countries have become interested in using waste from agriculture for power production, and dedicated energy crops are being developed in several countries. It is quite clear, though, that the increasing

global energy demand cannot be met with only biomass use. Still, the use of biomass can be increased significantly, and while efficiently used, it can play an important role in reducing CO_2 emissions globally.

1.1 Objectives of the thesis

The aim of this thesis is to study ash formation mechanisms during circulating fluidised bed combustion of solid fuels. The main emphasis is on determining the physical transformations of the ash-forming species. The understanding of ash formation and the subsequent behaviour of the ash particles is needed when developing combustion processes for solid fuels. The ash behaviour needs to be understood in studying the agglomeration of particles in the bed, the deposition of the ash particles on the heat exchanger surfaces in the furnace and in the convective pass, the usability of the possible sorbents and catalysts, as well as the operation of particle removal equipment and eventual hazardous emissions to the environment.

The thesis begins with a literature survey of fluidised bed combustion and ash formation during solid fuel combustion. The work concentrates on two solid fuels, a bituminous coal and wood-based biomass, which are introduced. The main characteristics of fluidised beds are described as are the particular features of fluidised bed combustion. The major ash formation mechanisms during pulverised coal combustion are reviewed based on the extensive literature available.

An experimental approach was chosen as a main method for this work. The experiments were carried out in full-scale operating fluidised bed combustion units. There were several reasons for this choice of method. Circulating fluidised beds are complex systems and while the hydrodynamics of the process has been successfully simulated in small-scale systems, mechanistic modelling of ash formation requires combination of the hydrodynamics of the bed, particle-particle interactions and combustion phenomena, including ash formation during combustion and subsequent transformations. Therefore, it is not surprising that no detailed mechanistic models of the ash behaviour during fluidised bed combustion have been published. Only recently, have mechanistic models on the ash formation during pulverised fuel combustion been presented

(Harb and Richards, 1991; Wilemski and Srinivasachar, 1994). Still, in the absence of the bed material, its movements and the interactions of the ash compounds with the bed, pulverised fuel combustion is a more simple process than fluidised bed combustion. Therefore, we believe that quite an extensive fundamental work is still required before ash formation during fluidised bed combustion can be mechanistically modelled.

Full-scale experiments were chosen because of the difficulties in scaling up the experimental results from laboratory scale devices. Even though several authors have presented scaling laws which can be used to scale-up fluidised bed reactors, these scaling laws are mostly concerned with replicating the hydrodynamic patterns of the bed. They do not consider the influence of combustion on the bed and particle behaviour or particle-particle interactions. Clearly, these are major issues when considering ash formation. The lack of understanding of these issues therefore leads to only limited understanding of scaling-up of the results from laboratory-scale reactors in regard to combustion and ash formation. While full-scale experiments suffer from lack of precise experimental data on several operational parameters, and they can only be conducted in very limited number of units with limited number of fuels, they are still needed to gain understanding of the fundamental phenomena affecting ash formation, to find the most crucial ash formation mechanisms, as well as to validate the results from laboratory- and pilot-scale reactors.

In this thesis, the comparison of the behaviour of ash during combustion of two very different fuels, coal and wood-based biomass, was carried out. Clearly, significant differences in the behaviour of the ash during the combustion of these two fuels are expected due to the different fuel characteristics, and in fact, differences have also been observed in operating plants (Raask; 1985; Anthony, 1995; Bryers, 1996; Miles et al., 1996; Skrifvars et al., 1998). This thesis studies the main ash formation mechanisms during circulating fluidised bed combustion of these two fuels. In addition, it describes the main differences in the ash behaviour with the two fuels, and explains some of the reasons for those differences.

2. Literature review

2.1 Solid fuels for energy production

The most commonly used solid fuels for energy production globally are coal and biomass, including agricultural waste. Solid biomass fuels are mainly used in the developing countries for heating and cooking providing approximately 35 % of their energy consumption (Bain et al., 1998). In industrialised countries, biomass has also traditionally been burned in home appliances, but in addition as a waste fuel from forest industry and agriculture. Lately, the use of biomass as a dedicated energy crop for electricity and heat production has raised interest in the countries trying to reduce CO_2 emissions from energy production (Evans, 1997). During coal combustion, the production unit size is usually relatively large. The major coal consumers are the industrialised countries, but the consumption is most rapidly increasing in countries such as China and India.

Many solid fuels which are used for energy production are based on waste materials. Such fuels include municipal solid waste (MSW), sewage sludge, pulp and paper industry wastes including black liquor, petroleum coke, waste coal, used tyres etc. While burning waste-based fuels, the primary goal is often to destroy the waste or reduce its quantity, and only as a secondary aim to produce energy. In fact, the energy production is often considered as an additional benefit, not a goal in itself. Of the above mentioned solid fuels, in this thesis, only coal and wood-based biomass are discussed.

2.1.1 Characteristics of wood and coal

Coal has been formed from plant materials, including wood, through peatification and coalification over long periods of time, often under high pressures and high temperatures (Bartok and Sarofim, 1991; Smoot, 1993). Peat can be considered to be an intermediate form of solid fuel between plant material and coal. Due to the formation of coal from biomass over a long time, the characteristics of wood and coal as fuels are quite different resulting in very different combustion characteristics.

Coals are commonly classified according to their rank. Rank basically describes the age of the coal, i.e. how far the coalification has advanced. The lowest coal rank is lignite which is brown to black in colour, and has a high moisture content and a low heating value when compared to higher rank coals. It still has recognisable woody material embedded in decomposed vegetable matter. Subbituminous and bituminous coals are black coloured, and show little woody material. Bituminous coals are more resistant to decomposition in air than subbituminous coals. They also have low moisture contents and high heating values. The highest rank coal is anthracite, which is hard and has low moisture and high carbon contents (Bartok and Sarofim, 1991).

While coal rank is an important determinant on the coal properties, also content of different macerals in the coals has been found to affect combustion behaviour. The most abundant maceral in coals is vitrinite, which makes up to 80 % of coal (Smoot, 1993). Other major macerals include liptinite and inertinite. The science which studies macerals in coals is called petrography (Bartok and Sarofim, 1991)

The heating value of coal is generally higher than that of wood, but also has a large variation with the coal rank. The heating values of coal are between 14–35 MJ/kg in dry fuel with 30 MJ/kg being a typical value for the exported bituminous coals. The heating value of wood is typically 20 MJ/kg in dry fuel (Nordin, 1994). Wood usually contains fairly large amounts of moisture, a typical value being 50 %, whereas coal moisture content typically stays between 2–20 %. The large moisture content of wood means that larger amount of fuel must be transported and fed into the furnace than during coal combustion. Also, combustion of very moist fuels may be problematic and has to be taken into account in the furnace design. The amount of oxygen in the wood is larger than in the coal; it is between 30–50 % in wood, and less than 25 % in coal. Also, the amount of volatile compounds is larger, and the amount of fixed carbon smaller, in the wood than it is in the coal. Therefore, wood particles are burned faster in the furnace and release heat faster than coal particles even though the high moisture content in the wood delays the drying and volatilisation processes.

In regard to the pollutant formation during combustion of wood and coal, sulphur content is usually negligible and nitrogen content fairly small in wood (Nordin, 1994; Turnbull, 1996) whereas the sulphur content in coals may be up

to 10 % (Bartok and Sarofim, 1991). The low sulphur and nitrogen contents in wood result in low emissions of sulphur and nitrogen oxides. It also provides an opportunity to use co-combustion of biomass to reduce SO_2 emissions from combustion of coal and other high-sulphur fuels (Nordin, 1995).

2.1.2 Ash-forming compounds in the solid fuels

Solid fuels contain inorganic constituents that form ash during combustion. These constituents are called *ash-forming compounds*. The ash-forming compounds may be found in the fuels as included and excluded mineral particles, salts, or organically bound into the fuel hydrocarbon matrix, Figure 1. The form of occurrence of the ash-forming species in the fuel affects the transformations of these species during combustion (Bool and Helble, 1995; Quann et al., 1990).
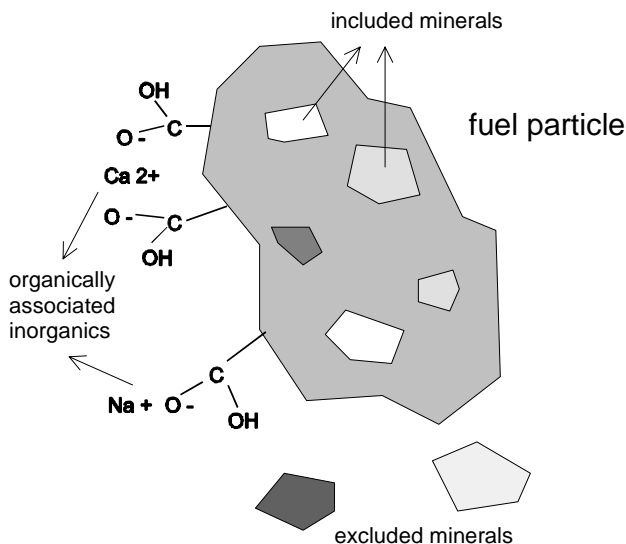

Figure 1. A fuel particle containing ash-forming constituents as excluded and included minerals as well as organically associated inorganics (adapted from Smoot, 1993).

The content of the ash-forming species in the solid fuels varies greatly. The older fuels contain typically more minerals whereas younger fuels contain a

major fraction of the ash-forming species as organically bound and as salts (Raask, 1985; Smoot, 1993; Turn et al., 1997). The amount of ash-forming compounds in the biomass fuels is typically less than 1 %, but can be as high as 10 % or more. The main ash-forming compounds in wood fuels are usually alkali and alkaline earth metals attached to the carboxyl groups of carbohydrates as metal-ions, or as oxalates and as carbonates (Nordin, 1994). In coal, a typical range of ash content is 5–15 %, but ash contents of up to 50 % may occur (Smoot, 1993). In general, high-rank coals contain most of the ash-forming compounds as minerals, whereas low-rank coals contain more organically bound inorganics. Typical minerals in coals are silicates (e.g. clays, quartz), carbonates (e.g. calcite, siderite), sulfides (e.g. pyrite) and oxides.

2.2 Fluidised bed combustion

Fluidised bed is a bed of solid particles suspended – or fluidised – by forcing air through them. In order for the bed to be fluidised, the air velocity has to be sufficiently high. The minimum value of the air velocity to cause fluidisation is called the *minimum fluidisation velocity*. When the air velocity is increased above the minimum fluidisation velocity, the air flows through the suspended bed as bubbles. This type of fluidised bed is called a *bubbling fluidised bed*. It has a clear bed region with a dense suspension, and a freeboard region with a low particle concentration. When the air velocity is increased, the particles are transported higher up in the reactor, and finally, when gas velocity exceeds a critical gas velocity, a condition is reached where the bed and freeboard regions can not be distinguished (Mori et al., 1992). A large fraction of the particles are elutriated from the bed, and circulated back to the reactor with a cyclone. This type of fluidised bed is called a *circulating fluidised bed*, Figure 2.

Fluidised beds have been used in the chemical industry since the early 1920's. The first coal combustion applications, however, were not developed until the 1960's even though the first patent on coal-fired fluidised bed boiler was applied two decades earlier (Pitrolo et al., 1987). The energy crisis in 1973 increased the interest of using coal as an alternative to oil, and fluidised bed combustion offered a way to burn coal in an environmentally more friendly way than conventional pulverised coal combustion. Later, fluidised beds have also

been successfully applied to combustion of alternative fuels such as biomass and waste materials.
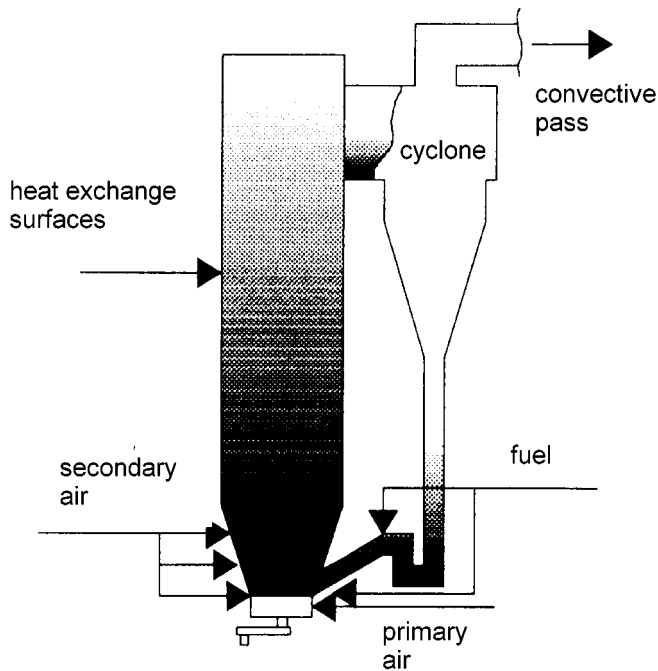
Figure 2. A schematic picture of a circulating fluidised bed boiler (adapted from Hyppänen and Raiko, 1995).

Fuel feed particle size is larger and fuel particle residence times in the hot-temperature zone are longer in fluidised bed combustion than in pulverised fuel combustion. A typical coal feed particle size in CFB combustion is 1–5 mm (Bartok and Sarofim, 1991; paper B) and during biomass combustion significantly larger (Valmari et al., 1998). Combustion temperatures and fuel particle heating rates in fluidised beds are significantly lower than in pulverised fuel combustion. Bed temperatures are typically around 1 100–1 200 K during combustion of coal and around 1 000–1 100 K during combustion of biomass. The temperature of burning particles exceeds the bed temperature with an average of 200–300 K, and with up to 500 K (Tang and Taylor, 1987; Hernberg et al., 1993). Hence, particle temperatures up to 1700 K may be reached.

Fluidised bed combustion has several advantages over the conventional combustion processes. The heat transfer in the bed is effective due to the large amount of solids. The relatively low burning particle peak temperatures and uniform sand temperature in the bed reduce the formation of NO_x. Sulphur oxide emissions can be reduced in fluidised beds by introducing sorbents, e.g. limestone, to capture sulphur. Furthermore, fluidised beds are flexible with regard to fuel. They can be used for combustion of fuels with varying combustion characteristics, making them an attractive alternative for biomass combustion as well as for the combustion of different waste fuels. Circulating fluidised beds have higher efficiencies and longer fuel residence times, and they are more efficient in sulphur capture than bubbling fluidised beds. The contact between gas and solid is good in the absence of large bubbles and in addition, they can handle solids with wide size and density distributions, and also have a wide operating range.

Fluidised bed combustion is a complex system with many interacting factors. In the absence of a fundamental understanding of some of the processes occurring during fluidised bed combustion, existing overall fluidised bed combustion models are combinations of physical models and empirical correlations (Brem, 1995; Wang et al. 1994; Azevedo et al. 1989). Much more experimental work is still needed to understand all the interacting factors and processes to develop purely mechanistic models.

Experimental work can be carried out in laboratory-scale and pilot devices, or full-scale operating reactors. Laboratory-scale and electrically-stabilised pilot-scale devices offer an opportunity to create well-controlled conditions inside the fluidised bed, and to study the influence of several variables on the phenomenon under consideration. In this way, mechanistic understanding of the processes in the fluidised beds can be acquired. However, the scale-up of fluidised beds, even though widely adapted, still can not adequately reproduce all the phenomena taking place in a full-scale reactor. While the hydrodynamics in the bed can be scaled-up (Horio et al., 1986), difficulties arise with particle flow patterns and density profiles as well as with the physical nature of solid particles, especially in circulating fluidised beds (Matsen, 1996). Therefore, while laboratory-scale experimental studies provide a superior way of gaining detailed mechanistic knowledge on the different phenomena taking place in the

fluidised beds, experimental data from full-scale reactors are needed to test the validity of the laboratory-scale devices.

The basic flow characteristics of the CFBs have been relatively clearly described in the studies, which have been carried out in small laboratory as well as large commercial reactors. The density of solids in a CFB decreases when rising within the reactor (Leckner and Andersson, 1992; Herb et al., 1992). Unlike in a bubbling fluidised bed, no gas bubbles with clear boundaries are formed. Instead, solids form denser islands, or clusters, which have a parabolic shape. At certain operating conditions, these clusters seem to have a rather uniform size, but widely varying velocity. The solids flow upwards in the middle of the reactor, but downwards close to the reactor walls (Horio and Kuroki, 1994). The solids downflow has been described as a fluid dynamic boundary layer by Leckner and Andersson, (1992). They also noted that the downflow was pronounced in the corners of a rectangular reactor, even though only in a small area. In the same study, they described a thermal boundary layer near the walls, which were covered with heat exchanger tubes. The temperatures of the boundary layer varied with time, which was caused by hot material flowing downwards close to the walls.

Combustion in a circulating fluidised bed occurs in all parts of the riser and the cyclones, but during coal combustion most of the fuel burns in the bottom part of the furnace (Lyngfelt et al., 1996; Wang et al., 1994). Operating experiences from pilot- and full-scale boilers have shown that a significant fraction of the wood-based biomass fuels burns in the upper parts of the furnace and in the cyclone. This can be explained by the high moisture content of the fuels resulting in long drying and devolatilisation times, and low density of the fuel particles making them follow the gas flow to the top of the furnace (Leckner, 1998). Consequently, the furnace top and cyclone temperatures can be 100–150 K higher than the bed temperatures during biomass combustion.

The conditions in the bottom part of a circulating fluidised bed reactor are mostly reducing. However, a fraction of the fluidising air by-passes the bottom part as relatively high-velocity voids. These jets of through-flowing air do not completely mix with the gas having a high content of combustible gas until further up in the furnace, and hence, they create temporary oxidising conditions in the bottom part of the furnace. Therefore, gas concentrations in the bottom

part vary between periods of oxidising and reducing conditions with the reducing condition still being dominant. The atmosphere in the upper parts of the furnace and in the cyclone loop is mainly oxidising (Leckner, 1998).
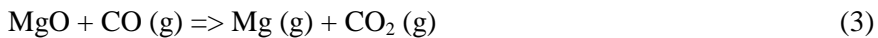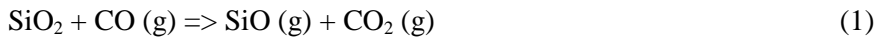
2.3 Ash formation

2.3.1 Ash formation during pulverised fuel combustion

The ash particle formation in conventional pulverised fuel combustion has been studied extensively in both laboratory scale devices and full-scale boilers. With these studies, a fairly thorough understanding of the ash transformation mechanisms has been gained. In the lack of such an extensive understanding of the ash transformations from other solid fuel combustion processes, we use here the knowledge on pulverised fuel combustion as a basis for the present study on fluidised bed combustion.

In pulverised fuel combustion, the fuel particles are injected into the furnace along with air through burners. The fuel particles are small, typically less than 100 μm in diameter during coal combustion (Bartok and Sarofim, 1991) and somewhat larger during biomass combustion. At the burner exit, the fuel and air mix in the furnace, the fuel particles heat up rapidly, they dry and devolatilisation starts (Saastamoinen and Richard, 1996). The combustion of devolatilised gases creates a flame front surrounding the fuel particle and little oxygen can penetrate through the flame into the fuel particle. When exiting the burners, the fuel particles are relatively close to each other and the particle cloud creates a flame close to the burner entrance. After the volatiles flame is extinguished, oxygen is able to reach the fuel particle surface and char burning starts. The fuel particle temperature is highest during char burning and it may then exceed the surrounding gas temperature by several hundred Kelvin. The particle temperatures at this stage may reach 2250 K in commercial furnaces (Bartok and Sarofim, 1991; Kjäldman, 1993).

Most of the ash transformations take place during char burning. A fraction of the ash-forming compounds is *volatilised* and released to the gas phase, Figure 3. The volatilised fraction depends on the fuel characteristics, combustion temperature and the gas atmosphere (Taylor and Flagan, 1982; Senior and

Flagan, 1984; Quann et al., 1990). The high combustion temperature and reducing atmosphere enhance volatilisation. Even elements present as refractory oxides such as SiO_2, CaO and MgO with very high melting and boiling temperatures may volatilise in the reducing conditions inside the burning char. This occurs by the reduction of the oxides to more volatile suboxides or metals:

$$SiO_2 + CO\ (g) => SiO\ (g) + CO_2\ (g) \tag{1}$$

$$CaO + CO\ (g) => Ca\ (g) + CO_2\ (g) \tag{2}$$

$$MgO + CO\ (g) => Mg\ (g) + CO_2\ (g) \tag{3}$$

The volatilised fraction is typically from one to a few percent of the total amount of ash during pulverised combustion of high-rank coals, and up to 10 % during combustion of low-rank coals. In biomass combustion, the volatilised fraction can be significantly higher (Christensen, 1995). Fuel type and characteristics, as well as ash composition greatly affect the volatilisation behaviour of ash-forming compounds. Especially, the extent of volatilisation largely depends on the form of occurrence of the ash-forming species in the fuels (Lindner and Wall., 1990; Quann et al., 1990; Jakob et al., 1996). Typically, ash compounds which are found as included and excluded minerals are not easily volatilised whereas the ash compounds which are found as organically-bound and as salts are readily volatilised during combustion.

During pulverised fuel combustion, the volatilised ash compounds form new particles in the boundary layer of the burning char particles by nucleation. Nucleation is induced when the volatile suboxides and metals are transported through the char boundary layer into the oxidising gas conditions of the furnace. The reduced compounds are oxidised, and since the equilibrium vapour pressures of the resulting oxides are much lower than the equilibrium vapour pressures of the reduced compounds, the oxidation results in very high supersaturation ratios. This induces immediate nucleation of the oxides in the char boundary layer (Quann and Sarofim, 1982; Senior and Flagan, 1982). The particles then grow by coagulation, condensation, and agglomeration. The resulting ash particles are small in size, usually $D_p < 1$ µm. These particles form a so-called *fine particle mode* in ash size distributions. Fine particle mode, which is formed by nucleation, is typically very narrow.
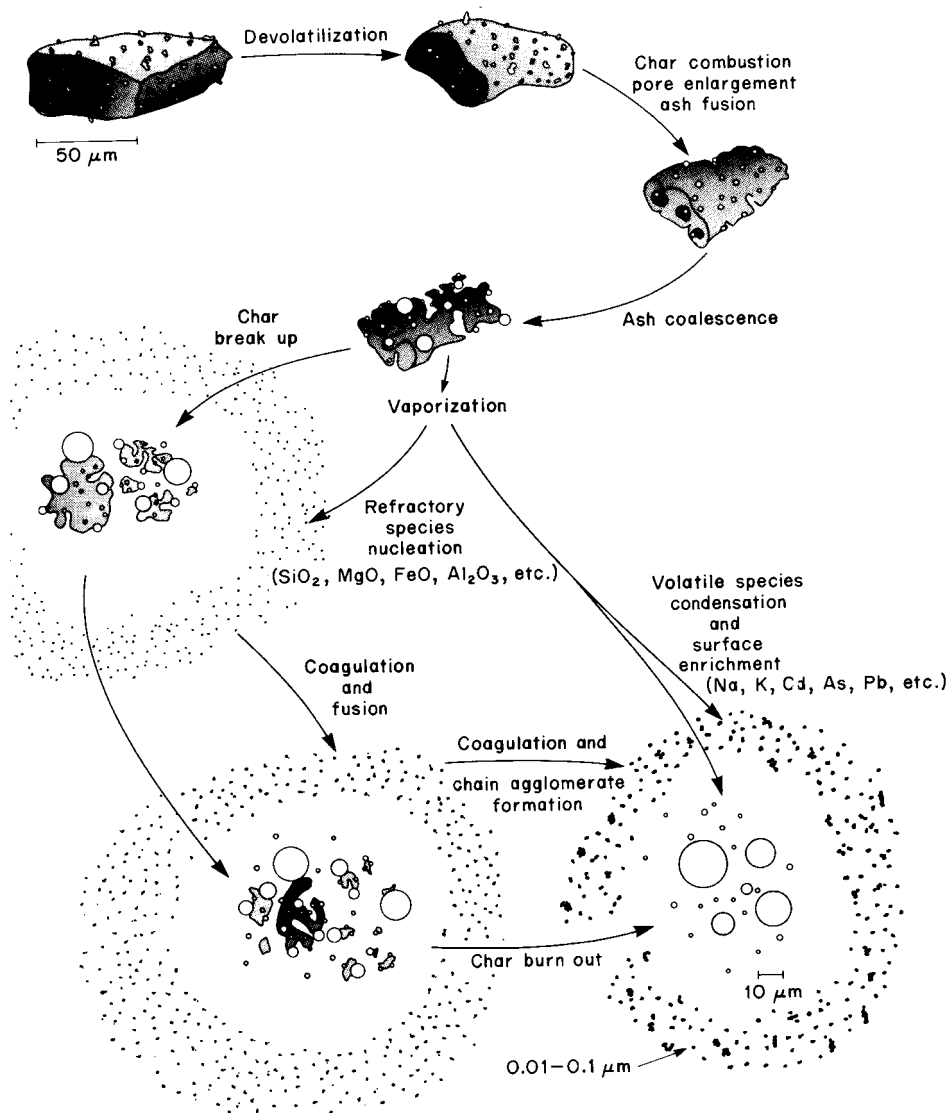
Figure 3. Schematic diagram of the processes involved in ash particle formation during pulverised coal combustion (Flagan and Seinfeld, 1988).

The compounds remaining in the char form *residual ash particles* inside the char particle and on the char surface (e.g. Wornat et al., 1995; Baxter et al., 1997; Olsson et al., 1997; McElroy et al., 1982; Markowski et al., 1980; Quann et al. 1990; Linak and Peterson, 1986; Flagan and Taylor, 1981). The formation mechanisms of residual ash particles depend upon the fuel, and the occurrence

of ash-forming compounds in the fuel. Mineral particles, which are often abundant in high-rank coals, usually melt and coalesce inside and on the surface of the char particles. This results in ash particles with a wide range of compositions depending upon the compositions of the parent mineral particles. Some minerals tend to avoid coalescence in the char, and consequently, their composition remains almost unchanged throughout the combustion process resulting in ash particles with compositions similar to the parent mineral particles. The existence of these ash particles however, depends also upon the fuel characteristics and the combustion conditions, e.g. temperature. Some of the minerals in the coals are extraneous, i.e. they are not associated in the coal macerals. These excluded minerals heat up during combustion and undergo chemical reactions and oxidation. They may also fragment due to rapid heating (Helble et al., 1990; Srinivasachar et al., 1990a; Srinivasachar et al., 1990b). Typically, they are fairly large in size (tens of micrometers), and formed ash particles are included in the residual fly ash fraction.

During low-rank coal and biomass combustion, the organically-bound ash-forming compounds coalesce to form beads on the char surface which may vary from submicron size to diameters of several micrometres (Quann and Sarofim, 1986; Wornat et al., 1995). The beads coalesce on the char surface and are released from the char as residual ash particles during char burn-out. The existence of the fine ash particles which are formed by nucleation and the coarse residual ash particles result in a *bimodal size distribution* of the combustion fly ash.

During pulverised fuel combustion, the only particle-to-particle interaction of the fuel particles and the ash particles occur with other fuel and ash particles in the furnace. Once the ash is formed inside the boundary layer which surrounds the char, the fly ash particles follow the gas flow into the heat exchanger section and into the particle removal devices. The particles may collide and attach to each other in the flue gas, but for the collision frequency to be significant and to affect the particle size, the number concentration of the fly ash particles has to be very high, on the order of 10^8 particles/cm^3. Only fine fly ash particles ($D_p < 1$ μm) are present in the combustion flue gases in such high particle concentrations, and therefore, the particle collisions in the flue gas may significantly affect only the fine mode particle size distributions.

The size and composition of residual fly ash particles ($D_p > 1$ µm) are predominantly determined already inside and on the surface of the burning char particle due to coalescence of ash-forming compounds to form ash particles. The size of ash particles formed from mineral particles is greatly affected by fragmentation of the char during combustion (Kang et al., 1990). For an easily fragmenting fuel, only one mineral particle may become trapped inside one fragment, and one ash particle results from this one mineral particle. If the fuel particle does not fragment during combustion, all the mineral particles inside one fuel particle may coalesce to form one ash particle. Therefore, either one ash particle is formed from one mineral particle, or one ash particle is formed from all the mineral particles inside one fuel particle. Naturally, anything between these two extremes is also possible (Smoot, 1993). The inorganically bound ash-forming compounds may either be released to the gas phase or coalesce and react with the mineral particles and with each other.

Certain phenomena affecting the size and composition of the residual ash particles, in addition to fairly infrequent collisions, may also occur in the post-combustion region in the furnace. Firstly, the volatilised compounds may react or condense on the surfaces of the ash particles and change the surface composition of the ash particles. Secondly, certain compounds may be released from the ash particle surface and react further in the gas phase and thirdly, oxidation reactions of the ash particles may continue in the post-combustion region (Quann et al., 1990).

2.3.2 Fuel particle burning in fluidised beds

When fuel particles are fed into a furnace, they undergo the same combustion stages as during pulverised fuel combustion, i.e. drying, devolatilisation, volatiles burning and char combustion. Due to large fuel particle size and relatively low temperature, the combustion stages during fluidised bed combustion are overlapping. When the surface of the fuel particle has dried and devolatilisation starts, the centre of the particle is still undergoing drying (Agarwal et al., 1986; Wildegger-Gaissmaier and Agarwal, 1990). Similarly, char combustion may start before devolatilisation has been finished (Saastamoinen et al., 1993). However, similar to pulverised fuel combustion, most of the ash is released from the fuel during char combustion (Manzoori and

Agarwal, 1992; Valmari et al., 1996), even though release of more than 60 % of Cl has been observed during pyrolysis in single coal particle tests (Manzoori and Agarwal, 1992).

Much lower particle temperatures, longer residence times and larger feed particle sizes in fluidised beds as compared to pulverised fuel combustion can be expected to have a strong influence on ash formation. For instance, lower particle temperatures can suppress the volatilisation of the ash-forming species, and fewer molten phases are formed. Larger feed particle size may be assumed to create larger ash particles. Additionally, important for ash formation, are the interactions of ash and fuel particles not just with each other, but also with bed material. These interactions may be chemical reactions of the ash-forming species with bed particles, or physical interactions of ash-forming species with bed material.

2.3.3 Ash formation due to collisions in the bed

In contrast to pulverised fuel combustion, a dense bed consisting of bed particles surrounds the fuel, char and ash particles in a fluidised bed. In addition to the interaction of the ash and fuel particles with each other, they interact with bed particles. Since the bed suspension is fairly dense - cross-sectional averages in CFBs typically 1 to 60 kg m^{-3} (Leckner and Andersson, 1992) – particle collisions are far more frequent than in pulverised fuel combustion. In fact, fuel only makes up a very small fraction – 1–2% – of the bed inventory, and therefore collisions of ash and fuel particles mainly occur with bed particles. Frequent collisions cause two competing phenomena to take place in the bed: fragmentation and agglomeration both of which affect particle size. Fragmentation decreases the size of particles in the fluidised bed whereas agglomeration increases the size of these particles.

Frequent collisions of the particles in the bed cause fragmentation of the fuel, char, ash and bed particles (Sundback et al., 1984; Arena et al., 1990; Chirone et al., 1991; Chirone et al., 1997). During combustion, mechanical fragmentation of char particles is small compared to fragmentation caused by combustion (Arena et al., 1990). However, pure mechanical fragmentation of ash and bed particles is significant, and has a major impact on coarse ash particle formation

(Latva-Somppi, 1997). The rate of mechanical fragmentation of particles in the bed is influenced by several variables, e.g. superficial gas velocity and material strength (Ayazi Shamlou et al., 1990).

Agglomeration of the ash and bed particles occurs by attachment of particles to each other in collisions. Particles in the fluidised bed are divided into four categories according to their tendency to attach to each other in a collision, i.e. according to their cohesiveness (Geldart, 1986). Only recently, has the bed behaviour of cohesive particles been simulated (Iwadate and Horio, 1998). Since during combustion, the ash particles are typically prone to attach to the surface of bed material particles (Latva-Somppi, 1998; Manzoori and Agarwal, 1993), the bed can be described as being comprised of cohesive particles and the cohesiveness may have a significant influence on the hydrodynamics in the bed. Bed and ash particle compositions, as well as bed temperature, have a major influence on the cohesion strength of the particles in the bed (Nordin et al., 1996).

Particle residence times in circulating fluidised bed boilers depend on the particle size and can be rather long. The size of circulating particles is determined by the cyclone cut-size, which is dependent upon the density of the particles, the gas velocity in the cyclone and the cyclone design. Particles smaller than the cyclone cut-size are transported to the convective pass through the cyclone whereas larger particles are separated in the cyclone and returned to the furnace through the return loop. The residence time of the large particles which are cycled many times through the cyclone back to the furnace can be several hours, or even days (Lyngfelt and Leckner, 1992).

2.3.4 Ash related problems during fluidised bed combustion

The smooth fluidisation of the bed is essential for efficient and effective operation. It ensures good contact between the particles, and consequently, efficient heat transfer in the bed between the particles and the heat exchanger surfaces. If the particles in the bed are sticky, or cohesive, as they usually are during combustion, it may result in the formation of small volumes in the bed that are not totally fluidised, i.e. they are defluidised. The heat transfer in these defluidised volumes decreases, and the decreased heat transfer results in higher

temperatures. The higher temperatures increase the stickiness of the particle surfaces and hence, the defluidised volume increases. Finally, if the temperatures become sufficiently high and the particles more sticky, the particles form large agglomerates which can eventually block the air flow in the bed and the whole bed is defluidised. This can happen during combustion if the combustion temperature is high, and the ash particles on the bed particle surfaces stick together and sinter to form hard bridges between the particles (Grubor et al., 1995; Lin et al., 1997; Latva-Somppi, 1998). The agglomeration temperature of the bed depends on the composition of the ash that is attached to the bed particles.

Bed and ash particles may attach to the heat exchanger tubes in the furnace walls and the flue gas channel (e.g. Skrifvars et al., 1994; Bryers, 1996; Miles et al., 1996; Michelsen et al., 1998). If the particle layer on the heat exchanger tubes grows thick, it will reduce the heat transfer from the flue gas to the tubes. This reduces the efficiency of the boiler. Usually soot-blowing and other means are used to remove the particle layers from the tubes, but sometimes the deposits grow so strong and tenacious that they can not be removed by usual means. The deposits may even grow so thick that they block the gas flow between the heat exchanger tubes and cause mechanical stress to the tubes. In this situation, the boiler has to be shut down and the deposits removed. The ash layer may also cause corrosion of the heat exchanger tubes and in the worst cases, the tubes have to be replaced (Anthony, 1995; Bryers, 1996). Bed and ash particles may also attach to surfaces other than the heat exchangers. For instance, in circulating fluidised beds, particles may attach to the walls of the cyclone return loop and the cyclone leg causing a deposit growth to occur there. This may cause blocking of the solids flow and material erosion in the return loop.

The particle emissions from combustion processes depend on the way of combustion, the resulting composition and size distributions of the fly ash particles, as well as on the flue gas cleaning. The amount of fly ash particles in the flue gas varies greatly depending on the ash content of the fuel and the combustion technology. In most fluidised bed facilities, a particle removal device is needed before the flue gases can be emitted through the stack into the atmosphere. Such devices are for example cyclones, fabric filters and electrostatic precipitators. A fraction of the fly ash particles penetrates the removal equipment and is emitted to the environment. For instance, electrostatic

precipitators have a penetration window in the particle size range 0.1 to 1.0 μm (Porle et al., 1995). In the atmosphere, the particles may travel long distances and eventually be inhaled by humans (Hinds, 1982). The fine particles have been found to be harmful to humans even in relatively small concentrations (Pope et al., 1995). The tendency of the volatile toxic compounds to be enriched in the fine particles is expected to enhance their harmful effects when inhaled.

3. Methods

3.1 Fuels and furnaces

The results and conclusions in this thesis are based on experimental work, which was carried out at two full-scale CFB boilers. The results on coal combustion are from two experimental periods, which were carried out in March and August 1990, in Pori, Finland, during combustion of Venezuelan bituminous coal. The boiler was commissioned in 1987 to produce a maximum of 28 kg/s steam with a temperature of 525°C and a pressure of 85 bar (papers A–D).

The experiments during combustion of biomass fuels were carried out at a combined heat and power plant in Nässjö, Sweden, with the capacity of 26 MW heat and 9 MW electricity. Two biomass fuels were investigated: forest residue and willow (Salix). The experiments during combustion of forest residue were conducted in March-April, 1996, and the experiments during combustion of willow in March, 1997 (papers E–H).

3.2 Experimental methods

Ash behaviour was studied using the methods of traditional ash sampling and aerosol technology. In traditional ash sampling methods, samples of ash are collected from different ash streams of the boiler. The typical collection streams are the fuel feed, sorbent or bed material feed, boiler bottom ash, and the fly ash collected possibly in several places in the boiler. The methods of aerosol technology enable sampling of particles directly from the flue gas flows and therefore, it is possible to determine the size distributions of the particles as they are in-duct. In addition, by analysing the elemental contents of the particles, the concentrations of different ash compounds in the flue gas can be determined as a function of particle size. Aerosol instrumentation that was used in this work, includes several measurement devices:

A *cyclone* can be used to collect coarse particles (papers A–H). The size of the particles collected in the cyclone can be varied by changing the flow in the cyclone. In this work, cyclone aerodynamic cut-sizes D_{50} between 1–8 μm were

used. Usually, a cyclone was used as a precutter device prior to the impactor to collect coarse fly ash particles.

A multi-stage *low-pressure impactor* (LPI) separates aerosol particles according to their aerodynamic diameter in the size range 0.02–15 µm (papers A–H; Kauppinen, 1992; Hillamo and Kauppinen, 1991; Kauppinen and Pakkanen, 1990). Collected samples can be weighed and analysed to obtain the mass and elemental particle size distributions.

A *differential mobility analyser* (DMA) was used to determine the number size distributions of the particles (papers A, C, D). A DMA size-classifies particles according to their electrical mobility in the size range 0.01–1 µm. Particles size-classified with a DMA were counted with a *condensation nucleus counter* (CNC). Prior to the measurement with a DMA-CNC system, flue gases were diluted with clean air due to the high particle concentrations in the combustion flue gases (Joutsensaari et al., 1994).

An *electrical low-pressure impactor* (ELPI) was used to determine the number size distribution of fly ash particles in the aerodynamic size range 0.03–2 µm (Keskinen et al., 1992). It was also used to monitor changes in the combustion process by measuring concentrations of different sized particles in real-time. An ELPI consists of a charger and a low-pressure impactor. Particles entering the ELPI are charged, and then collected in the low-pressure impactor according to their aerodynamic mobility. When the particles hit the impactor stage, they are discharged and the current is measured with electrometers attached to each stage. The current is then converted to particle size distributions.

In sampling from high temperatures, a *dilution probe* was used to dilute and cool sampled flue gas (papers E–H). The dilution air was fed into the probe through a porous tube to avoid particle losses during dilution and cooling.

The particle morphology and composition were studied with a *scanning electron microscopy* (SEM). Samples for the SEM were collected in several ways. Fly ash samples collected in the electrostatic precipitator (ESP) and in the low-pressure impactor as well as bottom ash samples were used from the coal combustion unit (papers A and B). During biomass combustion, samples were

collected at the ESP inlet after dilution of the flue gas and at the cyclone outlet directly from the flue gas channel (papers F and G).

Computer controlled scanning electron microscopy (CCSEM) was use to analyse large number (1 000–2 000) of individual particles for their size and composition. Minerals in the Venezuelan coal, as well as fly ash and bottom ash from coal combustion were characterised using the CCSEM.

4. Bottom ash formation - results and discussion

In earlier studies on bottom ash formation during fluidised bed combustion of Australian low-rank coal in a laboratory fluidised bed reactor, Manzoori and Agarwal (1992; 1993; 1994) found the residual ash to form a molten layer on the char surface as observed with traditional SEM imaging. From the char surface, residual ash was deposited on the bed particles by purely physical phenomena. The molten layer that was formed on the bed surface contained discrete mineral particles. In full-scale studies on combustion of different biomass-based fuels and sludge, Latva-Somppi (1998) found that the layers on the bed particles were not molten. Instead, the layers consisted of small ash particles. Ash fragments were released from the bed particle surface due to attrition (Latva-Somppi, 1997).

Bed material agglomeration and fragmentation depends on the type of bed material that is used. Different bed materials can be used depending on the fuel, availability of the bed material and process-related factors. In this study, we consider 'the bed material' to mean particles that are fed into the furnace in addition to the fuel even though the fraction of the 'bed material' were actually smaller than the fraction of ash in the bed. This is the case during coal combustion, where usually the ash content in the coal is so high that no additional bed material is needed to maintain an adequate bed inventory. Only possible sorbent is fed in addition to coal. Therefore, in this study we call sorbents 'bed material'. Typical bed materials during coal combustion are calcite and dolomite sorbents which are used to capture SO_2. During CFB combustion of coal, the bed is mostly made up of ash, and sorbent may only constitute a minor fraction (paper B).

During biomass combustion, sulphur content in the fuel, and consequently SO_2 concentration in the flue gas is usually so low that no sorbents are needed. Typical bed materials are sand particles. For example, quartz and illite sands are widely used bed materials. The fraction of the bed material as compared to the ash in the bed depends upon the fuel, the sorbent, the age of the bed, and the operating conditions of the furnace.

Bottom ash is formed from bed particles, which grow too large to be fluidised. Bed particles grow by agglomeration with other bed particles, as well as attachment of ash particles on bed particle surfaces. The ash forming compounds may become attached to bed material particles by two different mechanisms: i) deposition of the ash particles onto the bed material surface in collisions, or ii) a chemical reaction of the volatilised ash species with bed particles. The first mechanism results in the growth of the particles, whereas the latter mechanism usually does not affect bed particle size. The relative importance of the different growth and ash attachment mechanisms depends on the fuel and sorbent as well as combustion process characteristics (Latva-Somppi, 1998).

4.1 Bottom ash formation during coal combustion

4.1.1 Agglomeration of the ash particles

The major fraction of the bed typically consists of ash particles during CFB combustion of coal. In our study, approximately 80 % of the bed consisted of ash, about 19 % of reacted and unreacted sorbent particles, and about 1 % of the bed was coal. This was also approximately the composition of the bottom ash (paper B). The majority of bed particles were formed by agglomeration of coal minerals both inside the char particles and due to collisions in the bed. Therefore, the resulting bed particles were mainly agglomerates containing many mineral particles. This could also be seen from the wide variety of compositions of bed particles as presented in paper B. The compositions did not show any specific elemental concentrations indicating chemical reactions leading to the formation of the particles. Instead, for example bottom ash particles in an elemental normalised Ca-Si-Al ternary plot had a whole 0–100 % range of Ca contents (paper B). Obviously, this could not be due to a chemical reaction but instead, it was due to the agglomeration of particles with different compositions with each other.

Magnesium containing particles were an exception according to results in papers A and B. Mg was almost entirely found in the particles in association with Si, or Si and Al. In these particles, Mg content was always 15–20 %. Since Mg was not found with Si or Al in the coal minerals and only in small amounts

in the sorbent, the occurrence of Mg in the silicate and alumino-silicate particles was due to a chemical reaction of Mg with the ash particles. The reaction occurred inside the burning char particle.

Limestone sorbent particles were fed into the furnace to capture SO_2. In the furnace, sorbent particles calcined resulting in a porous particle structure, which was prone to fragmentation. A major fraction of the sorbent was fragmented, and particles became fine enough to penetrate the cyclone and consequently, form fly ash. The remaining sorbent particles stayed in the bed and the cyclone loop. Small fragments of sorbent particles were attached to ash particles in collisions. This was evidenced by a wide variety of bottom ash particles with mixed compositions rich in Ca. However, according to particle size distributions of bottom ash and feed sorbent, a large fraction of sorbent which stayed in the bed was not fragmented to any larger extent before being removed with the bottom ash (paper B).

Ash and sorbent particles making up the bed were not sticky, and hence, no agglomeration problems occurred in the furnace. This was due to the high melting temperature of ash and sorbent. In addition, no low-melting species were formed during combustion or in the bed. Consequently, coarse bed particles were easy to remove from the bed as bottom ash. This is typical for coal fired fluidised beds where the bed material seldom causes operational problems due to agglomeration of the bed or deposition on the furnace walls.

4.1.2 Chemical reactions of the volatilised species

Chemical reactions of the volatilized ash forming species with bed particles, in a circulating fluidised bed, may take place in the reducing conditions in the dense bed area at the bottom of the furnace (Lyngfeld, et al., 1996), or they may occur higher up in the furnace and in the cyclone loop where the atmosphere is mainly oxidising. Chemical reactions of volatilised species with bed particles are widely used in coal combustion, where sorbents are used to capture SO_2. Large sorbent particles stay in the bed until they fragment into smaller particles which penetrate the cyclone and escape with the fly ash, or until they agglomerate with bed particles to be large enough to be removed from the furnace with the bottom ash. SO_2 capture is based on a chemical surface reaction, which can be

simplified in the following way when limestone (calcite $CaCO_3$) is used as a sorbent:

$$CaCO_3 => CaO + CO_2 \hspace{4cm} (4)$$

$$CaO + \tfrac{1}{2} O_2 + SO_2 => CaSO_4 \hspace{3cm} (5)$$
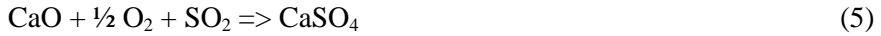
Reaction rate is dependent upon the temperature and gas atmosphere surrounding the reactants (Lyngfeld and Leckner, 1998). In addition, the surface area of the particles is important. In the case of calcite sorbent to capture SO_2, the volume of CaO is smaller than $CaCO_3$, and the volume of $CaCO_3$ is smaller than $CaSO_4$. Hence, the specific surface area of sorbent increases during calcination (4), but decreases during sulfation of CaO (5). The decrease in the specific surface area during sulfation may lead to a blocking of the pores in the sorbent particles and, consequently, decreased SO_2 capture efficiency of the sorbent.

Residence time is also a crucial factor on sulphur capture. In paper B, the sorbent particles in the bottom ash had much higher sulphur capture efficiency than the sorbent particles in the fly ash. The Ca/S ratios for fly ash and bottom ash were 6 and 3, respectively. This was presumably due to the much longer residence times of bottom ash particles in the furnace than those of fly ash particles (Lyngfeld and Leckner, 1992).

Other ash forming species than SO_2 may also react with sorbent particles, e.g. Cl forming $CaCl_2$, but little data are available on these reactions from real scale furnaces. In this study, no other species than SO_2 reacted with sorbent particles in the bed. Potassium was slightly enriched in the bottom ash which may have been due to a reaction of gas phase K with the ash particles in the bed. However, no conclusive results could be obtained.

4.2 Bottom ash formation during biomass combustion

4.2.1 Deposition of the ash particles on the sand

Wood-based biomass fuels contain relatively small amounts of ash-forming compounds. Therefore, an additional bed material, normally sand, is needed to maintain the bed volume at a desired value. The bed material interacts with the ash in the bed by chemical reactions and by physical collisions. Collisions of bed sand particles with ash and char particles result in the attachment of ash particles on the bed particles, resulting in the formation of a porous ash layer on the surface of bed sand particles, Figure 4. Closer study of the ash layer reveals that ash is deposited on the sand surface as particles, and no signs of molten ash are found. During combustion of forest residue, the ash layer was rich in non-volatile ash compounds, e.g. Ca and Si. The ash layer did not contain K or Na. Contrary to coal combustion, sulphur was not retained in the bottom ash. Both sulphur and chlorine were found to be volatile, and only very small amounts of sulphur and practically no chlorine were found in the bottom ash (papers E and G).
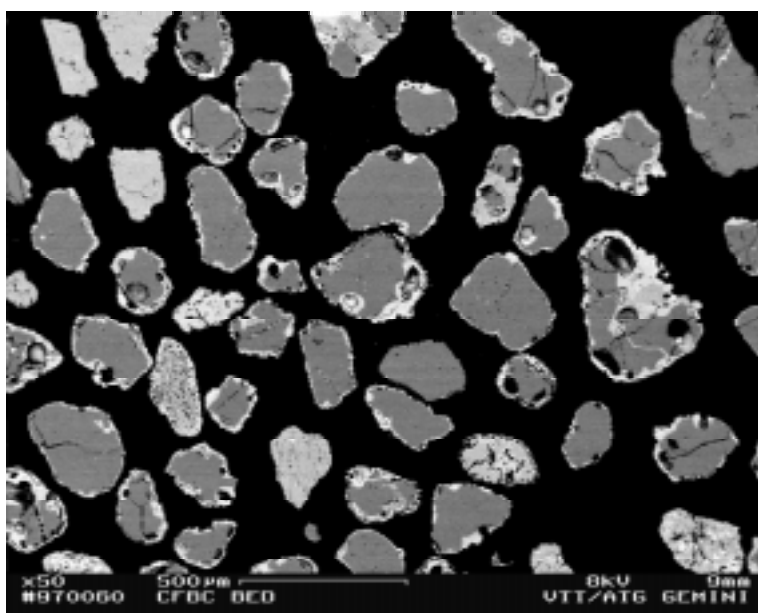

Figure 4. A back-scattered electron image of bed sand particles from CFB combustion of forest residue. The lighter grey shows the ash coatings on the sand particle surfaces (Lind et al., 1997).

As ash particles continue to collide with and attach to bed particles, the ash coating grows thicker. Eventually, bed particles grow too large to be fluidised due to a thick ash layer. The bed particles will then stay in the bottom of the furnace, and are finally removed as bottom ash.

The thickness of the ash layer on the sand particles depends on many factors such as the characteristics of the ash and sand, the age of the bed, and the flow fields in the furnace. In our studies, the ash fraction in the bottom ash was approximately 10 % during combustion of forest residue, and 20–25 % during combustion of willow. During combustion of forest residue, the bed was changed more frequently than usual, and therefore, the ash fraction in the bottom ash was presumably lower than is usual with this fuel. The whole year average from the same power plant gave a value of approximately 25 % ash in the bottom ash when using mainly forest residues as fuel (Nilsson et al., 1998).

4.2.2 Enrichment of the volatilised species

During combustion of biomass fuels, volatilised potassium reacted with sand particles which were used as bed material (Lind et al., 1997). Volatilised potassium seemed to diffuse into the bed particles and react with silicates and alumino-silicates, Figure 5. This resulted in the enrichment of K in the bottom ash as seen in papers E and G. Potassium is known to decrease the melting temperature of silicates. Therefore, the reaction may lead to lower melting temperature of the bed and, subsequently, bed agglomeration. In this study, however, no evidence of increased bed agglomeration tendency was observed due to enrichment of potassium in the sand.

Enrichment of Zn in the bed was observed during combustion of forest residue in paper F. We concluded that the retention was due to a chemical reaction of volatilized Zn with bed particles. Other heavy metals in the study (Cd, Pb and Cu) were not enriched in the bed material. However, small amounts of Pb and Cu were present in the bottom ash, and therefore, they may have reacted with bed material to a limited extent. Their presence in the bottom ash may have also resulted from the attachment of Pb- and Cu- rich particles on the bed material.
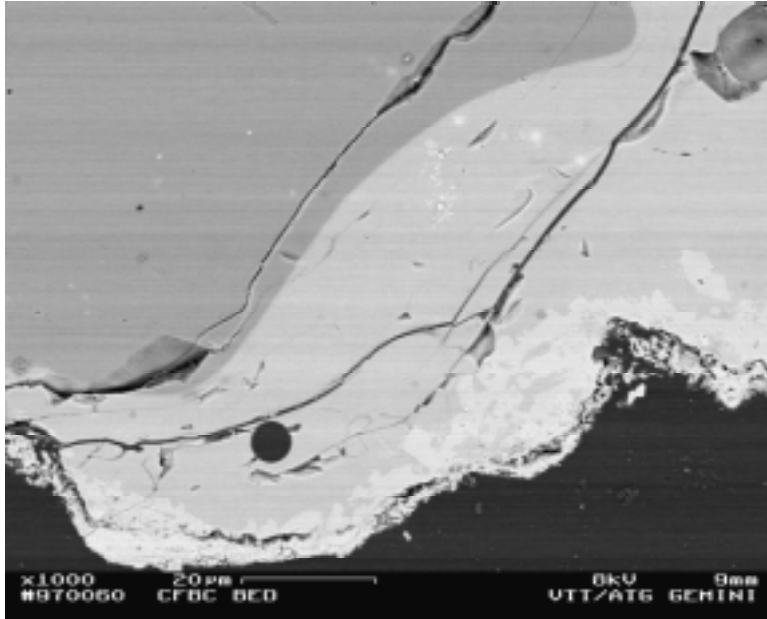
Figure 5. A back-scattered electron image of a bed sand particle from CFB combustion of forest residue. The dark grey in the upper left corner shows pure quartz and the lighter grey shows the area where the quartz has reacted with potassium. The lightest areas in the bottom part of the figure are ash particles attached to the sand particle surface (Lind et al., 1997).

In the future, if heavy metal concentration limits will be implemented for the biomass fly ash, retention of Zn in the bed may prove beneficial. Since Zn concentration in fly ash diminishes as a consequence of retention in the bed, the concentration may remain below the concentration limits. In this case, no further Zn reduction in the fly ash would be needed. Similarly, the capture of other volatile heavy metals in the bed by chemical surface reactions or adsorption in the sorbents may become necessary in the future to reduce their contents in the fly ash.

5. Fly ash formation - results and discussion

The same fly ash formation mechanisms as described for pulverised fuel combustion – fine ash particle formation by nucleation, and coarse particle formation as residual ash – take place during fluidised bed combustion. In addition, the bed material contributes to fly ash formation as bed particles break due to collisions, and some of the fragments become small enough to escape the cyclone. Therefore, fragments of bed material may be included in fly ash particles. Consequently, fly ash particles, during fluidised bed combustion, form by three different mechanisms: i) fragmentation of bed material, ii) residual ash particle formation inside the char particle and on its surface, and iii) volatilisation and new particle formation by nucleation. In the post-combustion region, fly ash particles may undergo transformations due to e.g. condensation of, and chemical reactions with, the volatilised species. As with pulverised fuel combustion, fly ash size distributions are bimodal. Fine mode is formed from nucleated particles and residual ash and fragmented bed particles together form coarse ash mode. In circulating fluidised beds, the upper size of coarse fly ash mode is determined by cyclone cut-size. Fuel characteristics and combustion conditions determine the other size distribution characteristics.

5.1 Fragmentation of sand and sorbent

During both biomass and coal combustion, a fraction of bed material fragmented in the bed and escaped the cyclone ending up in the fly ash. However, the extent of fragmentation was quite different in the two processes. Limestone sorbent in coal combustion fragmented extensively, and approximately 80 % of limestone which was fed into the furnace was present in the fly ash. This corresponds to about 25 % content of limestone in the fly ash. In paper B, computer-controlled SEM (CCSEM) analysis revealed a large number of fly ash particles with only Ca and Ca-S as main compounds indicating that sorbent particles did not agglomerate with ash particles before being removed from the furnace with the fly ash. The high amount of the sorbent ending up in the fly ash emphasises the importance of fragmentation behaviour of the sorbents. Easily fragmenting sorbents escape the bed and cyclone with only short times in the furnace for

sulphur capture whereas sorbents which do not readily fragment may have much longer times in the furnace resulting in better sulphur capture efficiencies. The short residence times of fine sorbent particles in the furnace are not usually entirely compensated with better SO_2 capture efficiency of sorbent particles with decreasing particle size.

Quartz sand used as bed material during combustion of forest residue and willow tended to fragment much less. Approximately 10 % of sand, which was fed into the furnace, escaped the cyclone with the fly ash. This was detected as a higher content of SiO_2 in the fly ash than in the fuel ash in papers E and G. The bed material content in the fly ash was approximately 5–15 %, and it was higher during combustion of willow than during combustion of forest residue. In the fly ash, Si was mainly found in the largest particles. The calculated amounts of bed material in fly ash are only estimates because the existence of Si in both the fuel ash and bed material, as well as simultaneous retention of fuel-originating Si in the bed and fragmentation of the bed material into the fly ash make the exact calculation extremely difficult.

Collisions of bed particles with each other also caused attrition of the ash layer which was formed on the surface of the bed particles. When the ash layer grew thick the collisions were strong enough to break the ash layer. Fragments of the layer became loose and were released to the bed as separate ash agglomerates. The extent of the breakage of the ash layer could not be studied in this case, but an earlier study in a laboratory reactor showed that the ash layer breakage produced ash particles even when fuel was not fed into the reactor (Latva-Somppi, 1997).

5.2 Residual ash

Residual ash is formed from ash forming species which do not volatilise during combustion. In pulverised coal combustion, these particles are mainly smooth and spherical, presumably formed from molten ash. Some large hollow particles, cenospheres, have also been observed. In this and earlier studies, residual ash particles from fluidised bed combustion of both coal and biomass differed completely from smooth spheres (papers A, B, E, G; Carpenter et al., 1980; Cheng et al., 1985). However, the formation mechanisms of these particles were

similar to the formation mechanisms of residual ash particles from pulverised combustion.

5.2.1 Coal combustion

Mineral particles in the coal formed small agglomerates, which contained a few mineral particles each as shown in paper A. The agglomerates formed inside and on the surface of char particles. They were exposed on the char surface with the char burn-out, and subsequently, they were either released to the furnace as separate agglomerates, or deposited on large bed particles by collisions of char particles with bed particles. Consequently, a fraction of the ash particles were removed from the furnace as bottom ash, and the majority was transported out of the furnace with the fly ash. Approximately 75 % of the minerals in the coal ended up in the fly ash along with the fragmented sorbent particles. Little agglomeration between the sorbent and ash particles was observed in the fly ash. In bottom ash, the agglomeration of ash particles with sorbent seemed to be more extensive. Residual ash particles showed little signs of melting during combustion. Only a few smooth spheres were found while the majority of particles were irregular, agglomerated particles as well as large porous, presumably sorbent, particles.

Based on the results in paper A, small mineral particles were released from the char without significant agglomeration. They formed an intermediate mode in the number size distribution at around 0.3 μm. The particles in this mode were irregular in shape, and the main ash elements in this size range were the same as the main elements in the coal ash, namely Ca, Si and Al.

5.2.2 Biomass combustion

Residual ash particles formed during CFB combustion of biomass were agglomerates consisting of primary particles up to several thousand in number, Figure 6, and presented in papers E, F, and G. Primary particle size was generally smaller than 1 μm. Primary particles in one agglomerate had varying compositions. Based on particle structure and the fact that a major fraction of the ash-forming compounds in the solid biomass fuels is found as organically-

associated (Baxter et al., 1998), we suggest the following formation mechanism for residual ash particles from CFB combustion of biomass: the organically-associated elements were released from the char structure, and they coalesced forming small beads on the char surface, as described by Wornat et al., 1995. These small primary beads then collided and agglomerated when the char burned out. The combustion temperature in the fluidised beds was so low and the residence time in the hot zone so short, that the beads did not have time to coalesce (Quann and Sarofim, 1982). Therefore, the beads retained their small size as primary particles and the particles remained agglomerates. In short, the particles were formed from the ash, which was left when the carbonaceous matter burned away from the fuel particles.
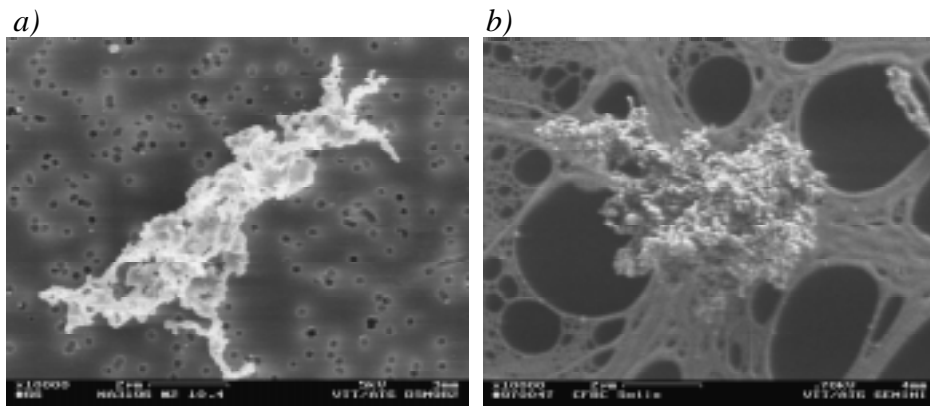
a)

b)

Figure 6. SEM micrographs of residual fly ash particles formed during CFB combustion of a) forest residue and b) willow (paper G).

After formation, some residual ash and char particles collided with bed particles in the furnace. Consequently, ash particles were deposited onto bed particle surfaces. The ash particles, which were not deposited on bed particles, were transported through the cyclone into the fly ash. This was the major fraction of the fly ash. Whether ash particles were deposited onto bed particles or not was presumably determined by the location, in the furnace, where the ash particles were formed. Moisture content in the fuels was fairly high as shown in paper G, and thus fuel particles took a long time to dry. Consequently, volatilisation and char burning can be expected to have taken place in the upper parts of the furnace and even in the cyclone. If ash particles were released from the char at this location, a high probability exists that ash particles escaped the cyclone

immediately after being formed and no collisions with bed material took place. In this case, ash particles retained their original shape in the absence of collisions which might have broken them. But, if instead the fuel particle burned in the denser bottom part of the furnace, ash particles collided with bed particles with a great probability. This resulted in the possibility of deposition of ash particles onto the surfaces of the bed material, and breakage of the agglomerates.

5.3 Fine fly ash particle mode

5.3.1 Nucleation

Nucleation (also called *homogeneous nucleation and homogeneous condensation*) is the formation of new particles from the gas phase without any pre-existing particles that can act as condensation nuclei. Particle formation by nucleation requires supersaturated vapours. This means that the saturation ratio of a vapour must be >1. Saturation ratio is defined as the partial pressure of the vapour p divided by its saturation vapour pressure p_s:

$$Saturation\ ratio = p/p_s \qquad\qquad (6)$$

Saturation vapour pressure is the partial pressure of a vapour when evaporation from a surface is in equilibrium with condensation onto the surface. Particles that are formed by nucleation are typically very small (10–100 nm). After formation and growth, they agglomerate to form long chains of fine particles during pulverised coal combustion (Helble et al., 1986; Kauppinen et al., 1996). Often, the mass concentration of fine particles has been considered to be the amount of ash that was volatilised during combustion (Quann et al., 1990). However, during fluidised bed combustion, a large fraction of the volatilised species was present in the coarse fly ash particles as a consequence of condensation and chemical surface reactions. Therefore, the volatilised fraction could not be determined based on the fine particle concentration. These phenomena are discussed in the following sections.

Nucleation of the volatilised ash forming species during combustion of biomass in grate-fired boilers was studied by Christensen, 1995. Volatilisation of the

ash-forming compounds, especially K, Cl and S, was extensive. Fine particles were formed by homogeneous nucleation of either salts of potassium or CaO. Nucleation was followed by rapid growth by condensation of potassium salts. This resulted in the fly ash particle fine mode at 0.2–0.6 µm with mass concentrations up to 2 g/Nm^3. The major fraction of the particle mass at this fine mode consisted of K, Cl and S. Contrary to the pulverised coal combustion, particles were mainly close to spherical in shape.

Nucleation of volatilised species during combustion can be studied by determining the number size distributions of the particles. Combustion-generated fly ash particle size distributions are usually bimodal. They have a significant nucleation mode in the submicron size range ($D_p < 1$ µm) and a major mass mode in the coarse fly ash particle size range ($D_p > 1$ µm). The number of particles in fine particle size mode is determined by particles that form by nucleation and their subsequent coagulation and agglomeration. A major fraction of the particle mass in this size range, however, may result from condensed species.

5.3.2 Nucleation during CFB combustion

The number size distributions of fly ash from CFB combustion of coal and biomass were determined using a differential mobility analyser (coal and forest residue) and an electrical low-pressure impactor (willow). The number size distributions were determined upstream of the particle removal devices after diluting the sample gas flow. Number size distributions during CFB combustion of coal, forest residue and willow are presented in Figure 7. The results for coal are given from three measurement days because a clearly decreasing trend in the concentration can be seen with time, as discussed in paper A. Particle size and concentration of size distributions were very stable during combustion of biomass. Clearly, the amount of nucleated particles at the ESP inlet is larger during the combustion of biomass fuels than coal, with approximately 2×10^5–2×10^6 particles/cm^3 with coal and 4–5×10^7 particles/cm^3 with forest residue and willow. The smaller number concentration during coal combustion may be due to two factors: i) smaller number of particles formed by nucleation, or ii) the nucleated particles are scavenged by the large particles in the bed.
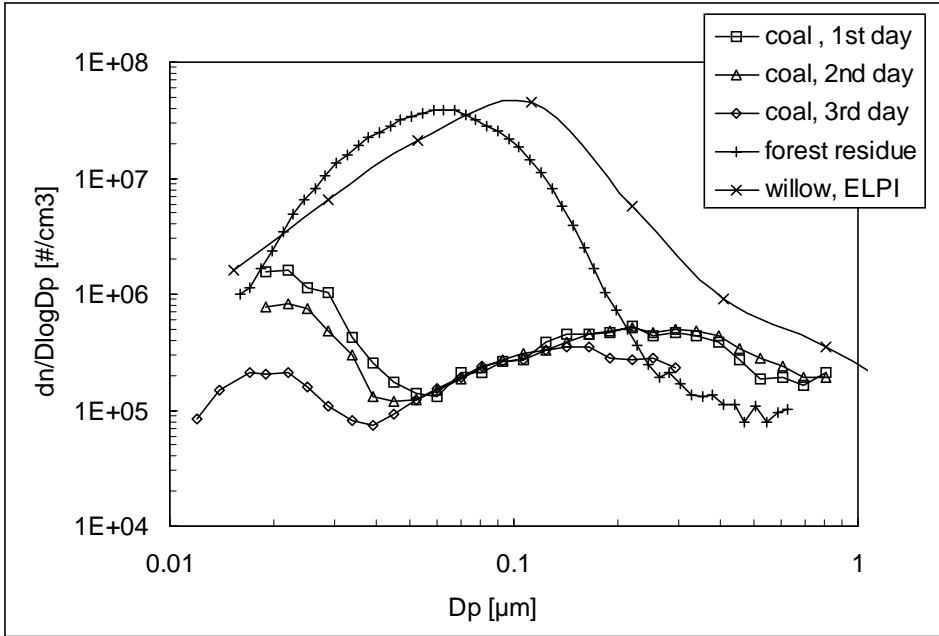
Figure 7. Number size distributions of fly ash particles in the submicron size range. CFB combustion of coal, forest residue and willow (paper A).

The nucleating species was presumably SiO_2 since Si showed a small peak at particle size distributions for particles $D_p < 0.1$ µm, both during combustion of coal and biomass. Si has also been observed in transmission electron microscope (TEM) studies of fine particles from bubbling fluidised bed combustion of other wood-based biomass fuels (Kurkela, 1998). The combustion temperature of coal is usually higher than that of biomass and therefore, Si volatilisation and subsequent nucleation would be expected to be more extensive. However, the number concentrations of fine particles during coal combustion are lower. This indicates that fine particles during coal combustion are scavenged by large particles in the bed, as suggested by option ii). This is plausible because coal usually burns in the lower parts of the furnace in the dense bed region whereas biomass tends to burn in the upper parts of the furnace and in the cyclone. Therefore, fine particles, which are formed during coal combustion, are scavenged by the large particles in the bed but the fine particles formed during combustion of biomass can escape from the furnace.

The size of the nucleated particles grows by condensation. Over 50% of the fine particle mass consisted of condensed species during biomass combustion. Based on papers E, G and H, the condensed species were mainly potassium chloride (forest residue) and potassium sulphate (willow). As a result of condensation, the fine particles were mainly spherical in shape, Figure 8, and papers E, F, and H. During coal combustion, the amount of condensing species was very low. Only Cl condensed on fine particles, presumably as HCl.

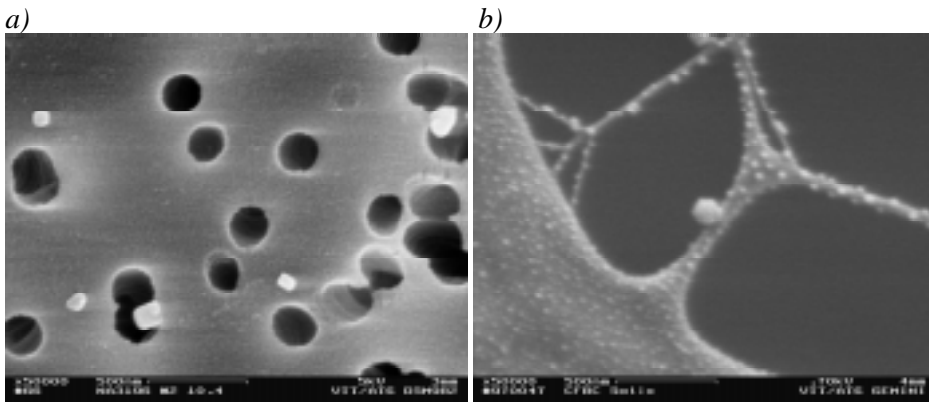*a)*   *b)*

Figure 8. SEM micrographs of fine particles formed by nucleation and grown by condensation during CFB combustion of a) forest residue and b) willow (paper F).

The mass size distributions presented in papers A, E, and G, Figure 9, showed that even though the number concentration of nucleated particles was high during CFB combustion of coal and biomass, they contributed very little to the overall particle mass concentration. The fraction of fly ash particle mass in fine particle mode was largest with willow, approximately 8 %, with 2 % in fine mode with forest residue and less than 0.3 % with coal. The importance of nucleation in fine mode formation can be seen when comparing the number and mass size distributions with the two biomass fuels. The number concentrations in both cases were fairly close to each other, but the mass concentration was almost triple in the case of willow. This indicates that seed particles were formed by nucleation of SiO_2, and the amount of seed particles was relatively constant with the two fuels. Mass concentration was determined by the amount of volatilised species prone for condensation which in the case of willow was significantly larger than with forest residue. This resulted in a more extensive

growth of fine mode particles during combustion of willow than during combustion of forest residue, and consequently, larger particle size and mass concentration of fine mode particles.
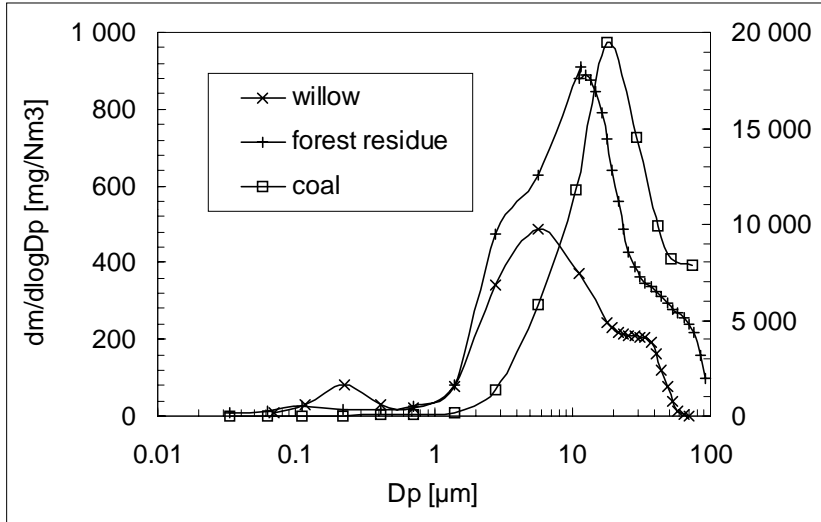

Figure 9. The overall mass size distributions of fly ash particles. CFB combustion of coal, forest residue and willow. For forest residue and willow: use the left y-axis, and for coal: use the right y-axis (papers A–C, E–H).

5.4 Condensation

Heterogeneous condensation is a process where particles grow by vapour deposition on the particle surface. With solid condensation nuclei, condensation may occur when the saturation ratio is greater than one. Saturation ratios of even a few percent greater than one may induce condensation. For particles in *the free molecular regime*, i.e. particle diameter D_p much smaller than the gas mean free path λ ($D_p << \lambda$), the growth rate of particles by condensation is governed by the rate of random molecular collisions of vapour molecules with particles. The net rate of arrival of the vapour molecules I to a spherical particle surface with diameter D_p is (Hinds, 1982):

$$I = \frac{\pi D_p{}^2 (p - p_d)}{\sqrt{2\pi m_v kT}} \propto D_p{}^2 , D_p << \lambda \tag{7}$$

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Net rate of arrival means the difference between the number of molecules that come to the surface and leave it. $(p–p_d)$ describes the difference of the partial pressure of the vapour in the gas p and the saturation vapour pressure on the particle surface p_d. Here p_d takes into account the Kelvin effect for small particles. m_v is the mass of a vapour molecule, T temperature, and k is Boltzman number.

In *the continuum regime* where particle diameters are much larger than the gas mean free path ($D_p \gg \lambda$), the net rate of arrival of vapour molecules I is governed by the diffusion of vapour molecules to the spherical particle surface:

$$I = \frac{2\pi D_p D_v (p - p_s)}{kT} \propto D_p, D_p \gg \lambda \tag{8}$$

Here $(p–p_s)$ describes the difference of the partial pressure of the vapour in the gas p and the saturation vapour pressure on the particle surface p_s. D_v is diffusion coefficient of the vapour. From eqs. (7) and (8) we see that the net rate of arrival of vapour molecules on the particle surface both in the free molecular and continuum regimes depends on particle diameter. In the free molecular regime the dependence is stronger with $I \propto D_p^2$ than in the continuum regime where $I \propto D_p$.

In regard to combustion, it is practical to study condensation by studying the concentration of the condensed elements in particles of different sizes. Concentration is given as the mass of a certain element m_i in a particle as compared to the total mass of the particle m_{tot}, i.e. concentration $= m_i/m_{tot}$.

The particle size dependence on the condensed species concentration can then be derived from eqs. (7–8):

$$I \propto D_p^2 \Rightarrow \frac{m_i}{m_{tot}} \propto \frac{I}{V_p} \propto \frac{1}{D_p}, D_p \ll \lambda \tag{9}$$

$$I \propto D_p \Rightarrow \frac{m_i}{m_{tot}} \propto \frac{I}{V_p} \propto \frac{1}{D_p^2}, D_p \gg \lambda \tag{10}$$

In (9) and (10), V_p is the particle volume ($\pi D_p^3/6$). Eqs. (9) and (10) are also valid for a gas-to-particle conversion which occurs by a fast chemical reaction

when the reaction rate is not the rate limiting factor. Then the reacting species are assumed to be evenly distributed in the particles.

Eqs. (9–10) assume particles to be spherical and that the size of a particle does not grow because of condensation. Accordingly, they can be used for elements that are present in small quantities in the vapour phase, e.g. trace elements during combustion of solid fuels. In pulverised coal combustion, the solid fuel combustion process, which has been studied most extensively, the major fraction of the ash forms residual ash particles. These particles are mainly spherical in shape, and formed from molten ash species. Therefore, the assumption of spherical particles is justified.

Eqs. (9) and (10) have been widely used in combustion studies when studying condensation of volatilised species on fly ash particles (Haynes et al., 1982; Neville and Sarofim, 1982; Neville and Sarofim, 1985; Linak and Wendt, 1993). During pulverised coal combustion, several elements have been shown to follow the particle size dependence given in these equations (Kauppinen and Pakkanen, 1990; Neville and Sarofim, 1985). In contrast, we did not find any elements that, during fluidised bed combustion in the coarse particle size range ($D_p \gg \lambda$), would have followed $1/D_p^2$ behaviour predicted by (10). Instead, as evidenced in papers A, E, G, and H, the concentrations of the major elements either decreased with decreasing particle size, or the increase with decreasing particle size was smaller than predicted by (10).

5.4.1 The effect of the agglomerate shape of the particles

The coarse fly ash particles ($D_p > 1$ µm) which were formed during CFB combustion of biomass and coal were not spherical. During CFB combustion of forest residue and willow, coarse fly ash particles were large agglomerates consisting of primary particles up to several thousand in number (papers E, F, and G). During CFB combustion of coal, the particles were irregular in shape, and some of them fairly porous (papers A and B). Clearly, the morphology of these coarse fly ash particles is completely different from the morphology of residual ash particles from pulverised coal combustion. Therefore, we studied the effect of the particle morphology on the gas-to-particle conversion of volatilised species, and the resulting concentration size distributions.

Agglomerate particles can be described as fractal-like structures, Figure 10. The particles are assumed to be agglomerates consisting of spherical primary particles with a uniform size with a diameter D_1. The mobility diameter of the agglomerate D_{aggl} replaces the diameter D_p of the spherical particle.
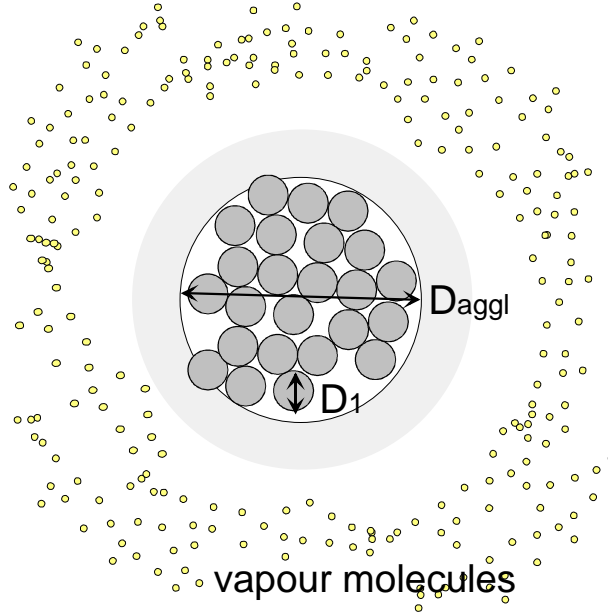

Figure 10. Schematic figure of an agglomerate particle with primary particle diameter D_1 and overall agglomerate diameter D_{aggl}.

For the agglomerates, the average number of primary particles N in an agglomerate can be written using a fractal-like dimension R_f in the following way (Lehtinen, 1997):

$$N = A \times \left(\frac{D_{aggl}}{D_1} \right)^{R_f} \tag{11}$$

In eq. (11), factor A is a constant. In the free molecular regime when $D_{aggl} << \lambda$, equation (11) is restricted to $R_f \geq 2$ if mobility diameter is used as D_{aggl} (Schleicher et al., 1995). In the continuum regime when $D_{aggl} >> \lambda$, eq. (11) holds also for $R_f < 2$.

The fractal-like dimension R_f describes the shape of a particle and the relative packing density of primary particles in an agglomerate. In general, the more compact the agglomerate, the higher is its fractal dimension. For any particles, $3 \geq R_f \geq 1$. For example, fractal dimension is 1 for an agglomerate forming a straight chain, 2 for a disk, and 3 for a dense sphere. Based on experiments and numerical simulations, an agglomerate which is formed by random diffusion-limited collisions of clusters in air in the absence of restructuring has a fractal dimension 1.6–2.2 (Lehtinen, 1997).

Using the description of agglomerates as fractal-like structures, and equations (9)–(11), we can derive the dependence of the condensed species concentration m_i/m_{tot} on particle size D_{aggl} for the agglomerates resulting from condensation. A similar dependence will result from any fast gas-to-particle conversion, i.e. also a fast chemical reaction, assuming the reacting species to be evenly distributed in the particles. Concentration dependence for the agglomerates can be written assuming a uniform primary particle size D_1 and fractal dimension R_f for a certain particle size range:

$$I \propto A_{aggl} \Rightarrow \frac{m_i}{m_{tot}} \propto \frac{I}{V_{aggl}} \propto \frac{A_{aggl}}{V_{aggl}} \propto \frac{N \times A_1}{N \times V_1} \propto \frac{A_1}{V_1} \propto \frac{1}{D_1}, \; D_{aggl} << \lambda \quad (12)$$

$$I \propto D_{aggl} \Rightarrow \frac{m_i}{m_{tot}} \propto \frac{I}{V_{aggl}} \propto \frac{D_{aggl}}{V_{aggl}} \propto \frac{D_{aggl}}{N \times V_1} \propto \left(D_{aggl} \right)^{1-R_f}, \; D_{aggl} >> \lambda \quad (13)$$

In (12) and (13), A_{aggl} is the area and V_{aggl} the volume of the agglomerate and N the number of primary particles with diameter D_1 in an agglomerate. For agglomerates with a uniform primary particle size and assuming the neck area between primary particles to be negligible:

$$A_{aggl} = N \times A_1 \tag{14}$$

$$V_{aggl} = N \times V_1 \tag{15}$$

For particles much smaller than the gas mean free path, eq. (12), the concentration of the condensed species does not depend on the size of the agglomerate, only upon the size of the primary particles. This assumes that the

diffusion inside the agglomerate particle does not limit the condensation. For agglomerates with large number of primary particles the diffusion inside the particle becomes significant and eq. (12) can not be used. Then the adsorption of the vapours is a complex result of variables such as the number of primary particles in an agglomerate, the adsorption probability of the vapours, the mean free path of the vapours, and the fractal dimension of the agglomerate (Rosner and Tandon, 1994).

The concentration of the condensed species increases with decreasing particle size for particles much larger than the gas mean free path, eq. (13), because for all the particles, $3 \geq R_f \geq 1$. The slope of the increase depends on the fractal dimension of the agglomerate and therefore, the formation mechanism of the agglomerates. In the special case when $R_f = 1.0$, $D_p \gg \lambda$, the concentration of the condensed species does not depend on particle size.

We have to note that equations (12-13) use *the mobility diameter D_{aggl}* of the agglomerates. In our measurements, however, we determined the concentrations of the different elements as a function of *the aerodynamic diameter D_{ae}* of the particles. In the continuum regime, where the slip correction factor can be considered to be unity, the relationship between the mobility and aerodynamic diameters can be written in a following way (Kelly and McMurry, 1992):

$$D_{ae}{}^2 \propto \rho_{eff} \, D_{aggl}{}^2 \tag{16}$$

Here, ρ_{eff} is the effective density of the particles. The effective density can be derived by writing mass of the particle; on the one hand, using effective density, and on the other hand, by using fractal dimension (Schleicher et al., 1995):

$$M \propto \rho_{eff} \, D_{aggl}{}^3 \tag{17}$$

$$M \propto D_{aggl}{}^{R_f} \tag{18}$$

From eqs. (17-18) we get for the effective density:

$$\rho_{eff} \propto \frac{D_{aggl}{}^{R_f}}{D_{aggl}{}^3} \tag{19}$$

Using eqs.(16) and (19), the relationship between the aerodynamic and mobility diameters of the particles can be expressed in a following way:

$$D_{ae}{}^2 \propto \frac{D_{aggl}{}^{R_f}}{D_{aggl}} \qquad (20)$$

By using aerodynamic diameter from eq. (20), eq. (13) becomes:

$$\frac{m_i}{m_{tot}} \propto \frac{1}{D_{ae}{}^2} , D_{ae} >> \lambda \qquad (21)$$

Consequently, when using aerodynamic diameter, the concentration of the condensed species does not depend on the fractal dimension when a uniform fractal dimension is assumed for a certain particle size range. Therefore, when using aerodynamic diameter, the particle size dependence should be similar to that for spherical particles.

5.4.2 Condensation during fluidised bed combustion

Chlorine was volatile during CFB combustion of forest residue and willow (papers E, G, and H). When the flue gas cooled down, Cl condensed on the fly ash particles mainly as KCl (paper H). The Cl concentrations, as determined after condensation in the dilution probe (papers E, G, and H), followed approximately $1/D_{ae}{}^{1.2}$ behaviour during combustion of forest residue and $1/D_{ae}{}^{1.0}$ during combustion of willow in the particle size range 0.5–5 μm, Figure 11. The concentration size distribution of chlorine during coal combustion (paper A) had a particle size dependence $1/D_{ae}{}^{1.2}$ in the continuum regime, Figure 12.

Evidently, the concentration of Cl does not follow $1/D_{ae}{}^2$ behaviour as given by eq. (21). Whereas the concentration does increase with decreasing particle size, the increase is significantly smaller than given by eq. (21). The most probable reason for the discrepancy between the experimental results and eq. (21) is the irregular shape of the particles (paper H). Possibly, the net rate of arrival of the vapour molecules onto the particle surface is not directly proportional to the particle mobility diameter, as assumed in eq. (13). In fact, while the agglomerate

particle mobility diameter has been used in describing agglomerates, also measures such as the effective outer radius have been used to determine the vapour flux due to diffusion (Rosner and Tandon, 1994; Schleicher et al., 1995). Therefore, other factors than the mobility diameter may have to be used to determine the vapour flux onto an irregular agglomerate particle surface. Clearly, when studying fluidised bed combustion, more research is needed to study the condensation of vapours onto the agglomerate particles, especially in the continuum regime.
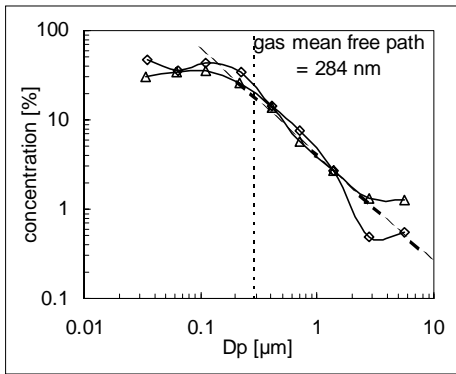
Forest residue   *Willow*
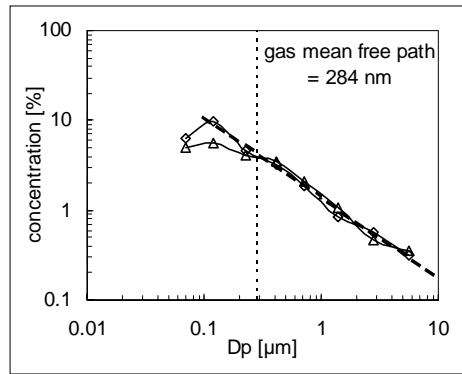

Figure 11. The concentration size distributions of Cl as measured during CFB combustion of biomass. The dashed lines denote the particle size dependencies $1/D_p^{1.2}$ and $1/D_p$ for forest residue and willow, respectively (papers G and H).

In the free molecular regime Cl concentration is so high – up to 30 % – that the particle size can not any longer be considered to be constant, but instead, grows due to condensation of KCl. Consequently, in this case eqs. (9) and (12) are not valid.

Some elements were partially volatile during combustion, followed by the condensation of the volatilised fraction. In this case, the concentration increased with decreasing particle size especially in the small particle size range ($D_p < 1$ µm). However, the increase was smaller than for chlorine. Partial volatilisation and subsequent condensation were observed for several elements: during combustion of forest residue K and Na (papers G and H), and during combustion of willow K, Na and S (papers E, G and H).
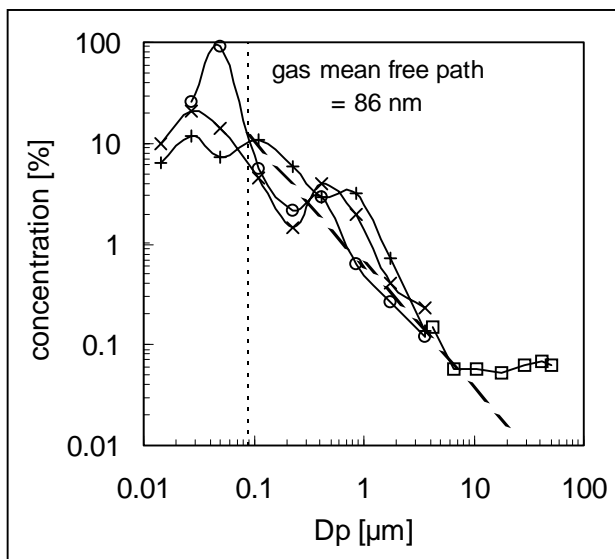
Figure 12. Concentration of Cl in fly ash particles during CFB combustion of coal. Dashed line depicts $1/D_p^{1.2}$ values (paper A).

During coal combustion, in addition to Cl none of the matrix elements showed even partial volatilisation. Instead, the trace elements Se, Sr, Mo, Cd and Sb showed partial volatilisation and subsequent condensation (paper D).

Four major sources of error were identified when determining the concentration size distribution curves: i) error of the elemental analysis, ii) error in the mass determination, iii) deposition of the particles in the wrong impactor stages due to diffusion, and iv) deposition of the particles in the wrong impactor stages due to particle bounce. i) and ii) affect mostly small particles where the total mass and the elemental mass are low. iii) and iv) distort the size distributions by depositing particles in the wrong impactor stages. The maximum error due to i) and ii) in this study was approximately 30 % for the smallest particle sizes, and less than 5 % for particles > 300 nm. In the case of biomass combustion, particle bounce and diffusion can be considered to be negligible due to the condensed KCl layer on the particles, and due to the relatively large particle size of the fine mode particles. During coal combustion, particle bounce was reduced by greasing the collection substrates, and by using double stages for stages 7, 8, and 9, where the mass concentration was highest. Consequently, particle bounce was considered insignificant for the concentration curves.

5.5 Gas-to-particle conversion by chemical reactions

The volatilised ash forming species are available for chemical reactions if they do not nucleate or condense after being exposed to the oxidising atmosphere outside of the burning char particle boundary layer. These species may then react with existing particles. We call this a gas-to-particle conversion by chemical reaction. For example, the use of sorbents for sulphur capture in fluidised bed coal combustion is based on the surface reaction of gas phase SO_2 with sorbent particles.

Chemical reactions of the ash forming species with existing particles may take place inside the burning char particle in the reducing atmosphere, or after being released from the char in the furnace. The reactions occurring inside the char particle result usually from the release of organically-bound inorganics when the carbon matrix burns away. Consequently, the inorganics are released from the structure and are prone to reactions. Especially when the equilibrium vapour pressure of the released species is low they tend to react already inside the burning char, as happens to organically-bound Mg during coal combustion. In other cases, the equilibrium vapour pressure of the released species may be so high that they are transported from the char into the furnace through the char boundary layer and still remain in the gas phase. In the mainly oxidising conditions in the furnace, the gas phase species may then undergo reactions with other gas phase species as well as existing particles.

Similar to gas-to-particle conversion by condensation, the concentration size distributions of the reacted species can be used to study gas-to-particle conversion by chemical reactions. A fast chemical reaction was described along with condensation in the previous section, and here a similar description is presented for a slow chemical reaction. In this case, the diffusion through the boundary layer and inside the particles is not limiting the reaction rate. Instead, the rate of conversion is controlled by the reaction rate, and the distribution of the converted species in the particles is controlled by the reacting, or effective, area of the particles A_{eff}. Because the effective area on the particle surface is controlling the size distribution of the reacting species, the size distributions resulting from a chemical reaction are similar whether the reaction takes place inside a burning char particle, or outside of the char. This is provided that the area of the ash particles does not change during combustion.

For spherical particles assuming the effective area to be evenly distributed in the particles, the gas-to-particle conversion by a slow chemical reaction results in the following size dependence of the reacted species:

$$I \propto A_{eff} \propto D_p{}^2 \Rightarrow \frac{m_i}{m_{tot}} \propto \frac{I}{V_p} \propto \frac{1}{D_p}, \qquad \text{for all values of } D_p \qquad (22)$$

Using eqs. (14-15) and (22), the concentration resulting from a slow chemical reaction on an agglomerate surface is found not to depend on the agglomerate particle size, only on the primary particle size. Concentration dependence for all particles becomes similar to eq. (12):

$$I \propto A_{aggl} \Rightarrow \frac{m_i}{m_{tot}} \propto \frac{I}{V_{aggl}} \propto \frac{A_{aggl}}{V_{aggl}} \propto \frac{N \times A_1}{N \times V_1} \propto \frac{A_1}{V_1} \propto \frac{1}{D_1}, \text{ all } D_{aggl} \qquad (23)$$

In (23), the reacting species are assumed to be evenly distributed in the primary particles and the diffusion inside the agglomerate can be neglected. Assuming the primary particle size to be constant in all the agglomerates, $1/D_1$ does not change with the agglomerate size. This result is similar to the results for porous particles presented by Linak and Wendt (1993). They claimed that the concentration of trace metals was independent of particle size if the volatile trace metals reacted with very porous particles so that diffusion inside the particles was not limiting the reaction rate. The internal surface area per unit mass was assumed independent of the particle size, basically the same assumption as made here when assuming the uniform primary particle size in the agglomerates.

5.5.1 Coal combustion

During fluidised bed coal combustion, several elements that are bound organically or as inorganic salts in the coal, are released from the char. They may react with mineral particles inside the char or be released to the gas phase. Coals contain usually relatively high concentrations of minerals as inherent and extraneous particles. During combustion of high-rank coal (papers A and B), organically- bound magnesium reacted with mineral particles inside the char. Also Na ended up in the coarse fly ash particles as a consequence of a chemical

reaction. However, this may also have happened after the volatilised Na was released to the gas phase where it reacted on the surfaces of the fly ash particles. Several elements (K, Ca) were found in the coarse fly ash particles due to their original occurrence in the coal minerals. These elements were not released from the minerals during combustion (papers B and C).

The major fraction of the sorbent ended up in the fly ash due to fragmentation. Similar to the sorbent in the bottom ash, also this sorbent fraction captured sulphur by a surface reaction. This resulted in the sulphur concentration which was relatively independent of particle size in the particles $D_p > 0.1$ μm, Figure 13. In these particles, sulphur was almost entirely present as $CaSO_4$. Interestingly, sulphur showed similar behaviour during combustion of forest residue even though no sorbent was used. The S size distribution was independent of particle size for particles $D_p > 0.1$ μm and the main S-containing compound was $CaSO_4$. In contrast to coal and forest residue combustion, the sulphur concentration during willow combustion showed a clear increase with particle size resulting from condensation of K_2SO_4 on the fly ash particles.

Coal   *Forest residue*   *Willow*
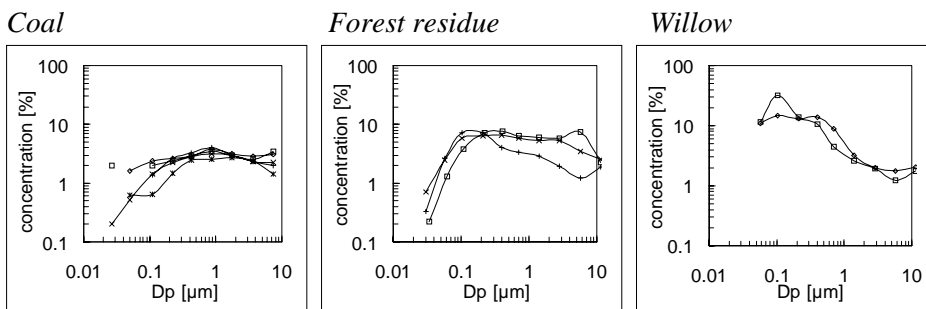
Figure 13. Concentration of sulphur in the fly ash particles from CFB combustion of coal, forest residue and willow.

5.5.2 Biomass combustion

Chemical surface reactions were the main gas-to-particle conversion mechanisms for all studied heavy metals Cd, Pb, Cu and Zn with both biomass fuels. The surface reactions were extremely effective in capturing the volatilised heavy metals into the coarse fly ash particle mode (paper F). Consequently, the heavy metals were not enriched in the fine particle fraction contradictory to all

the earlier studies on volatile heavy metal behaviour. According to speciation analysis of Cd in the willow combustion fly ash, the most probable surface reaction was that of Cd with silicates forming $CdSiO_3$ (Lind et al., 1998). Based on the same analysis, Zn was found as ZnO as very small (< 30 Å) particles or a very thin coating on the fly ash particles. Pb and Cu react readily with silicates based on equilibrium calculations and were assumed to be present as silicates in the studied fly ash (Nordin, 1998).

Sulphur behaviour was strongly dependent on fuel composition and process conditions. The gas-to-particle conversion mechanisms of sulphur during combustion of forest residue and willow were determined based on eqs. (21) and (23) as well as the behaviour of Cl. During forest residue combustion, the main gas-to-particle conversion mechanism of sulphur was a chemical surface reaction. Almost all sulphur in the fuel reacted with Ca-rich ash particles forming anhydrite ($CaSO_4$), and very little SO_2 (approximately 6 ppm). In contrast, during willow combustion, the main gas-to-particle conversion mechanism of sulphur was condensation. Approximately 50 % of sulphur formed potassium sulphates which condensed on the fine particles, and the rest of the sulphur stayed in the gas phase as SO_2 (papers F, G, and H), Figure 13.

The different behaviour of sulphur with the two fuels was probably due to the different conditions in the furnace. During willow combustion the gas atmosphere in the furnace was highly reducing with the CO concentrations over 500 ppm during almost the entire measurement period, whereas during forest residue combustion CO concentrations were somewhat lower with average values 100–200 ppm. Local reducing gas atmosphere resulted in the decomposition of $CaSO_4$ in the furnace (Lyngfeld and Leckner, 1998). Therefore, it seems likely that during combustion of willow, the gas atmosphere in the furnace was reducing hindering the formation of $CaSO_4$ and consequently, further up in the furnace SO_2 was available for reactions with K. During combustion of forest residue the conditions in the furnace were more oxidising, and the reaction of SO_2 with Ca in fly ash particles was possible. Due to the high concentration of Ca-rich fly ash particles, little SO_2 was left to react with K.

6. Conclusions and recommendations for future work

The formation mechanisms of bottom and fly ash during circulating fluidised bed combustion of two biomass fuels and a bituminous coal were determined based on experimental results. The experiments were carried out in full-scale operating boilers. The results of this thesis can be used to describe the ash behaviour in the fluidised bed boilers and therefore, to help solving ash-related problems while developing more efficient processes, and boilers for new fuels.

Figure 14 summarises the main ash formation mechanisms during coal combustion, as determined in this work. The main bottom ash formation mechanism was agglomeration of the coal minerals. Limestone sorbent was used to capture SO_2, and no additional bed material was used besides sorbent and the minerals contained in the coal. The bottom ash was formed mainly from large and agglomerated mineral particles, as well as some unfragmented sorbent. Some agglomeration of the fragments of limestone and minerals was observed. Sorbent particles, which were contained in the bottom ash, had a high SO_2 capture efficiency due to long residence times in the furnace and the cyclone loop. No other gas phase species other than SO_2 reacted with the sorbent particles. Slight enrichment of potassium in the bottom ash was observed presumably due to a surface reaction of volatile potassium with the ash particles in the furnace.

Fly ash had two particle modes, coarse and fine fly ash particles. The coarse fly ash was formed by fragmentation of sorbent in the bed and residual ash particles. A major fraction of the sorbent, approximately 80 %, ended up in the fly ash, while only 20 % was removed from the furnace in the bottom ash. Residual ash particles were formed inside and on the surface of the char particles by agglomeration of a few mineral particles originally contained in the coal. The resulting particles were irregular in shape showing almost no signs of melting of the minerals. Small mineral particles were released from the char without agglomeration. They formed an intermediate mode in the size distribution in the submicron size range at around 0.3 µm.
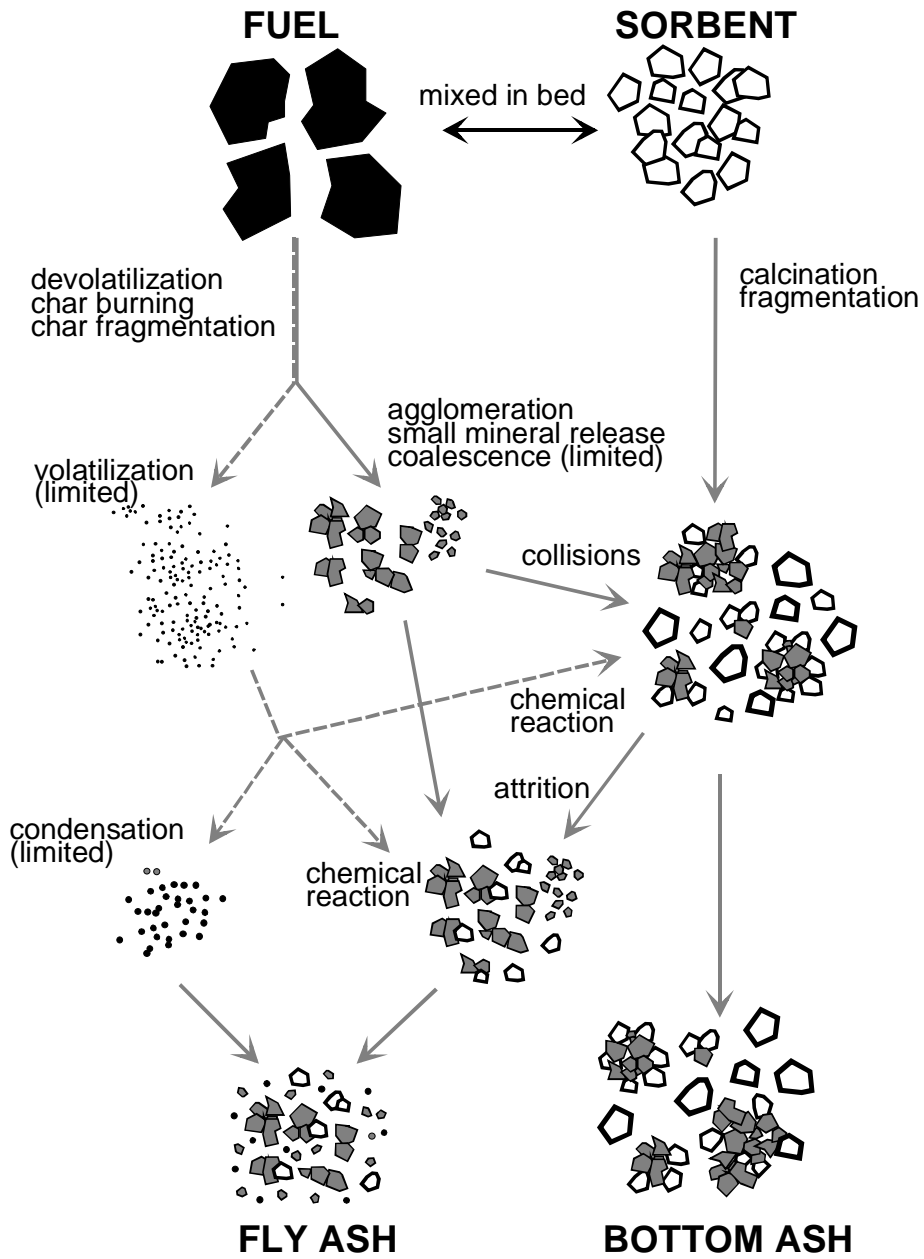
Figure 14. A simplified schematic figure of ash formation mechanisms during CFB combustion of a bituminous coal, as determined in this work.

The ash-forming compounds were mostly non-volatile, and less than 1 % of the fly ash particles were present in the submicron size range. The fine particle mode was presumably formed by nucleation of SiO_2. Its mass consisted mainly of condensed HCl. Sulphur was volatilised during combustion, and it was captured by limestone resulting in the occurrence of the major fraction of S in the coarse fly ash as well as bottom ash particles. The remainder of the sulphur was emitted as SO_2. Sulphur capture efficiency was 75–78 %. Heavy metals Se, Sr, Mo, Cd and Sb were partially volatilised, and subsequently, condensed on the particles resulting in a slight enrichment of these elements in the fine particle mode.

During biomass CFB combustion, Figure 15, the bottom ash was formed by the deposition of ash particles on quartz sand particles. The deposited particles were mainly non-volatile, Ca- and Si-rich particles. In addition, volatilised K and Zn diffused into and reacted with the bed sand. Bottom ash was depleted of volatile Cl, S and Cd. Approximately 25 % of the ash-forming species originating from the fuel were removed from the furnace with the bottom ash.

The fly ash size distributions were bimodal with a residual ash mode containing the major portion of the particle mass, and the fine particle mode containing 2–8 % of the particle mass. Residual ash particles were large agglomerates with up to several thousand submicron primary particles. They were formed inside and on the surface of fuel particles from the non-volatile ash compounds. A small fraction – approximately 10 % – of the bed sand fragmented and was found in the fly ash.

The fine particle mode was formed by nucleation of the volatile ash compounds, followed by growth by condensation. The nucleating species was presumably SiO_2. The condensing species were KCl with forest residue, and K_2SO_4 with willow. Fine mode particles were mainly individual, spherical particles. No agglomeration of the particles was observed.
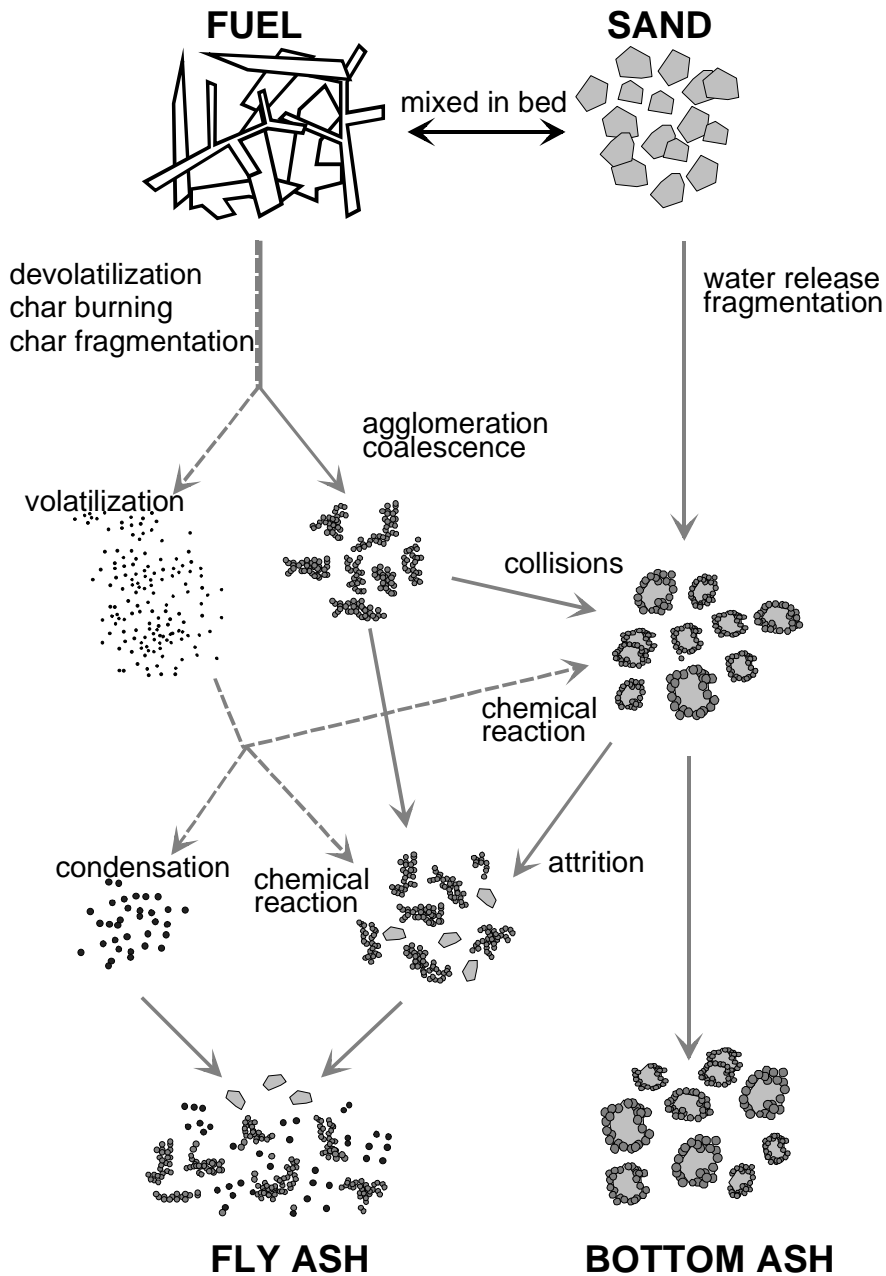
Figure 15. A simplified schematic figure of the ash formation mechanisms during CFB combustion of solid wood-based biomass, as determined in this work.

The effect of the agglomerate shape of the particles on the gas-to-particle conversion of volatilised species was studied by describing the coarse fly ash particles as fractal-like structures. The agglomerates had a primary particle diameter D_1, an agglomerate mobility diameter D_{aggl}, and a fractal-like dimension R_f. Based upon experimental results and the fractal-like structure description, the gas-to-particle conversion mechanisms of the volatilised ash compounds were determined. Condensation resulted in enrichment of the condensed species in fine particles whereas gas-to-particle conversion by a chemical surface reaction resulted in a concentration of the volatilised species, which did not depend on particle size. This is contradictory to earlier combustion studies where fly ash particles have been spherical, or close to spherical, and consequently, both chemical reactions and condensation have resulted in enrichment of the volatilised species in fine particles. During fluidised bed combustion, while volatilisation of the ash compounds was important in the formation of the bottom ash, fly ash characteristics were determined by the subsequent gas-to-particle conversion mechanisms.

Sulphur behaved in an entirely different way with the two biomass fuels. During combustion of forest residue, sulphur was captured in the coarse fly ash particles by a chemical surface reaction forming $CaSO_4$. Little SO_2 was present in the flue gas. During combustion of willow, sulphur reacted with potassium forming K_2SO_4 which condensed mainly on fine fly ash particles. In addition, approximately 50 % of the sulphur in the flue gas was in the form of SO_2. The different behaviour of sulphur with the two fuels was presumably due to different combustion conditions in the two cases. The gas atmosphere in the upper parts of the furnace was reducing during combustion of willow preventing the formation of $CaSO_4$ on the surface of the fly ash, and consequently, sulphur was available for the lower temperature reaction with potassium. The behaviour of sulphur is of great importance when studying the deposit formation on the heat exchanger tubes, as well as sulphur emissions with co-combustion of biomass and coal. Therefore, further studies should be carried out to determine all the factors influencing the reactions of sulphur with the ash compounds.

Volatilised heavy metals were effectively captured by the coarse fly ash particles by a chemical surface reaction during combustion of both forest residue and willow. None of the studied heavy metals showed enrichment in the fine particles. This is of great importance for the environmental consequences of

the heavy metals. First, conventional particle removal devices effectively capture the coarse fly ash particles and the heavy metals with them. Second, the solubility of the heavy metals in the environment depends on the speciation. Chemical reactions of the heavy metals result in the species, which are not easily soluble, and therefore this facilitates the recirculation of ash back into the forests. Third, coarse particles are not transported long distances in air and therefore, heavy metal pollution concentrates in the vicinity of the combustion facilities. Fourth, the coarse particles can not penetrate into the crucial parts of the lungs, i.e. alveoli, when inhaled by humans.

The basic ash formation mechanisms during fluidised bed combustion are presented in this thesis. In the future, more detailed knowledge should be acquired to determine the key characteristics of fuels and combustion processes affecting ash formation. In addition, further research is needed to determine the effect of the agglomerate structure of the particles. Such knowledge is necessary in order to develop experimental and modelling prediction methods of ash formation and transformations, which are needed when introducing new fuels and combustion processes. This detailed knowledge can be obtained from experimental work with laboratory-scale devices where process conditions can be controlled appropriately. The prediction tools should then be developed by combining the detailed experimental data with existing or entirely new combustion models. Eventually, this should result in mechanistic understanding of ash formation and transformations during fluidised bed combustion.

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