Fine particle emissions and slag formation in fixed-bed biomass combustion - aspects of fuel engineering

Jonathan Fagerström
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Abstract

There is a consensus worldwide that the share of renewable energy sources should be increased to mitigate climate change. The strive to increase the renewable energy fraction can partly be met by an increased utilization of different biomass feedstocks. Many of the "new" feedstocks puts stress on certain challenges such as air pollution emissions and operation stability of the combustion process. The overall objective was to investigate, evaluate, and explain the effects of fuel design and combustion control - fuel engineering - as primary measures for control of slag formation, deposit formation, and fine particle emissions during biomass combustion in small and medium scale fixed-bed appliances. The work in this thesis can be outlined as having two main focus areas, one more applied regarding fuel engineering measures and one more fundamental regarding the time-resolved release of ash forming elements, with particular focus on potassium.

The overall conclusion related to the abatement of particle emissions and slag formation, is that the release of fine particle and deposit forming matter can be controlled simultaneously as the slag formation during fixed-bed biomass combustion. The methodology is in this perspective denoted “fuel engineering” and is based on a combined approach including both fuel design and process control measures. The studies on time-resolved potassium release showed that a Macro-TG reactor with single pellet experiments was a valuable tool for studying ash transformation along the fuel conversion. The combination of dedicated release determinations based on accurate mass balance considerations and ICP analysis, with phase composition characterization by XRD, is important for the understanding of potassium release in general and time-resolved data in particular. For wood, the results presented in this work supports the potassium release mechanism from "char-K" but questions the previously suggested release mechanism from decomposition of K-carbonates. For straw, the present data support the idea that the major part of the potassium release is attributed to volatilization of KCl. To further explore the detailed mechanisms, the novel approach developed and applied in this work should be complemented with other experimental and analytical techniques.

The research in this thesis has explored some of the challenges related to the combined phenomena of fuel conversion and ash transformation during thermochemical conversion of biomass, and has contributed with novel methods and approaches that have gained new knowledge to be used for the development of more effective bioenergy systems.
Scientific papers

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


III. **Alkali transformation during single pellet combustion of soft wood and wheat straw.** Submitted to Fuel Processing Technology. Jonathan Fagerström, Erik Steinvall, Dan Boström, Christoffer Boman

IV. **Influence of kaolin additive on the release of ash forming elements during biomass combustion.** Manuscript. Jonathan Fagerström, Dan Boström, Christoffer Boman

V. **Semi time-resolved release of ash forming elements during single pellet combustion of biomass.** Manuscript. Jonathan Fagerström, Dan Boström, Christoffer Boman

VI. **Control strategies for reduction of alkali release during grate combustion of woody biomass - influence of process parameters and fuel additives.** Accepted for consideration in a special issue of Fuel Processing Technology. Jonathan Fagerström, Anders Rebbling, Joseph Olwa, Erik Steinvall, Dan Boström, Marcus Öhman, Christoffer Boman
Other contributions

Additional publications of relevance although not included in the thesis.

Peer-review papers


Conference proceedings


4. Slagging tendencies during combustion of different biomass fuels in two small scale (<50 kW) grate fired appliances - A substudy within the EU FP7-SME project AshMeIT. 21st European Biomass Conference and Exhibition - From Research to Industry and Markets. Copenhagen, Denmark, June 3-7, 2013. Rebbling A, Näzelius I-L, Fagerström J, Boström D, Boman C, Öhman M.


Technical reports


4. **Development of a combustion technology for small scale CHP based on externalfired gas turbine - Phase 2: Transference of alkali compounds to the exhaust gaseous during biomass combustion on a grate (< 300 kW) and deposition studies in a down stream high temperature heat exchanger.** Swedish Energy Agency Report nr P 31396-2, June 2011. Ma C, Öhman M, Olwa J, Fagerström J, Boman C.

5. **Forest Power, BotniaAtlantica.** 6 bulletines (one as a first author). 2011/2012.

1. Introduction

1.1 Background

Renewable energy is generally defined as energy converted from sources that are re-produced faster than they are consumed. The most common sources are wind, solar, hydro, geothermal, and biomass. According to the Renewable Energy Policy Network, renewable energy accounted for 19% of the global energy consumption in 2012 (figure 1).

\[\text{Figure 1. Estimated distribution of global energy consumption in 2012. Adapted from [REN21 2014].}\]

There is a consensus worldwide that the share of renewable energy sources should be increased to suppress climate change as it is considered one of the most urgent sustainability issues of our planet [Rockström et al. 2009]. Besides climate change, there are some other factors that have been recognized as motivation for an increased utilization of renewable energy, such as i) the depletion of fossil fuel resources [Höök and Tang 2013], ii) the energy supply security and political conflicts [UN 2013], and iii) the creation of job opportunities [Irena 2013].

Estimating the current use of biomass on a global level is difficult since some developing countries lack reliable data. Predictions into the future are even more problematic and estimations in the literature should therefore merely be taken as what if scenarios instead of actual predictions. A recent study [Slade et al. 2011] made a solid contribution by summarizing the existing data and presenting four what if scenarios for the biomass potential (figure 2). The least optimistic scenario was believed to be able to supply twice the
current bioenergy use (energy basis), and the most optimistic scenario was believed to be able replace and exceed all fossil fuels of today. The main reason for the large spread in potential was claimed to be related to the deployment of energy crops, which in turn is a function of available land area and production yield. Apparently, biomass has a considerable potential to increase its contribution to the primary energy supply. However, although aspects of, for example, sustainability for the energy crop cultivation and usage need further investigation before it can be applied in large-scale, the utilization of residues and waste for energy conversion most probably have room for expansion and should accordingly be used wisely.

Figure 2. Global biomass potential and associated agricultural, societal, and environmental conditions. Adapted from [Slade et al. 2011].

For Europe in particular, the potential for cellulosic residue and waste resources have been estimated by [ICCT 2014]. The estimation aimed at reflecting a sustainable contribution without major negative impacts on the environment or other business lines. A re-calculation of the annual resource amounts indicate that it is sufficient for year around production with more than 100 000 bioenergy plants with a size of 1 MW. Thus, it is notable that residues and waste streams have the potential to contribute substantially to the European energy supply.
Finally, the strive to increase the renewable energy fraction can partly be met by an increased utilization of different biomass feedstock alternatives.

1.2 Motivation

The combustion industry mutually agrees that the main challenge of biomass combustion today is an increased fuel flexibility. The strive to increase fuel flexibility puts stress on certain challenges such as air pollution emissions and operation stability of the combustion process. Many of the "new" opportunity fuels contain high amounts of nitrogen and ash forming elements that might cause an increase of gaseous and particulate emissions in comparison with traditional stem wood [Vassilev et al. 2010]. In line with that, the operation stability of the combustion process as e.g. deposit formation and corrosion are also affected by the ash forming elements [Bryers 1996]. The control of particle emissions and deposit formation were together, with the development of mathematical models for design and troubleshooting of combustion processes, identified as three key research areas for the fixed-bed fuel conversion technology [Yin et al. 2008].

Recently also the European Commission claimed that "urban air pollution" will become the top environmental cause of mortality worldwide by 2050 [EU clean air]. Moreover, the costs related to air pollution are huge and it was estimated that the total cost burden year 2010 caused by air pollution was 330-940 billion euro. As one of the attempts to abate this, two new legislations concerning solid biomass combustion have been announced; the Ecodesign legislation [Ecodesign 2014] that concerns small (<500 kW) appliances and the Medium scale combustion legislation [MCP 2013] that concerns appliances between 1 and 50 MW. An expected increased utilization of "new" biomass feedstock is also a driving force for enforcing these two legislations.

Fine particle (< 1 µm) emissions from combustion sources can be reduced by three principally different methodological measures; i) "pre-process" cleaning, ii) "in-process" cleaning, and iii) "post-process" cleaning. Pre-process cleaning, means that impurities and particle forming matter are removed from the fuel prior to combustion, and post-process cleaning (also denoted secondary measures), means that the particles are removed in the stack by technologies such as cyclones, electrostatic precipitators (ESP) and bag house filters. In-process cleaning (also denoted primary measures) means that the formation of fine particles is restricted/reduced through the capturing of certain ash forming elements as residual ash that is easily removed from the process by ash feeding systems. This methodology has so far not been implemented by the industry to any great extent, although some
initiatives have been undertaken, especially for the abatement of gaseous SO$_2$ emissions [Cheng et al. 2003]. However, the scientific data available are rather comprehensive and the knowledge in this field is in many aspects, ready for further development and implementation. Concerning particle emissions, the most crucial elements to control for most biomass fuels are potassium, sodium, and zinc [Obernberger et al. 1997, Boman 2005]. The behavior of these elements, with respect to melting and decomposition temperatures, as well as vapor pressures and thermal stability for their respective compounds, are set by the fuel (ash) chemical composition and the combustion process conditions [Baxter et al. 1998]. The term "fuel engineering" is used here to describe the methodology by which the combination of fuel design and process control is applied to control the behavior of the elements which form fine particles and deposits.
1.3 Objectives

The overall objective with the research presented in this thesis was to investigate, evaluate, and explain the effects of fuel design and combustion control - fuel engineering - as primary measures for control of slag formation, deposit formation, and fine particle emissions during biomass combustion in small and medium scale fixed-bed appliances.

The specific objectives of the thesis, as corresponding to the separate papers, were to:

I. Determine the influence of peat ash composition on particle emissions and slag formation in grate biomass co-combustion. Emphasis was put on ash chemical behavior in general and potassium fractionation in particular. (Paper I)

II. Perform a comprehensive synthesis to determine critical ash forming processes and compositions in fixed-bed combustion generalized for phosphorus-poor biomass fuels. This was done by a systematic review of data and experience gathered from fixed-bed combustion experiments of 36 different biomasses, including chemical analysis of their bottom ashes and slags. (Paper II)

III. Determine the release of major ash forming elements after both the devolatilization phase and the char combustion using single pellets of soft wood and wheat straw. (Paper III)

IV. Determine the influence of kaolin addition on the release of ash forming elements and on the formation of residual ash. (Paper IV)

V. Determine the semi time-resolved release of K, S, and Cl for two different biomass fuels (energy wood and wheat straw) by off-line residual ash analysis, and to determine the phase composition in the residual ash to enable a discussion regarding the K-release mechanisms. (Paper V)

VI. Explore primary control strategies for reduction of the release of K, Na, and Zn from the fuel bed during grate combustion of woody biomass, by determination of the influence of both process parameters and fuel additives on the ash transformation in general and the release behavior of alkali and zinc in particular. (Paper VI)
2. Scientific background

2.1 Biomass as a fuel

2.1.1 Feedstock categories

Today there is no universal classification system of the biomass resources but most studies include the feedstock classes: forest residues, agricultural residues, waste, and energy crops. Primary forestry is not included in all biomass potential assessments due to the risks associated with decreasing biodiversity and carbon sinks upon extensive utilization. The usage of peat for energy is heavily debated and its carbon neutrality questioned, but nevertheless peat is included in this work as a biomass feedstock used for fuel blending. Energy crops are usually divided into first and second generation crops where the former constitutes conventional food crops and, the latter, of non-edible crops. The ideal energy crop is basically a non-edible species that produces high yields on marginal and degraded land. From a historical perspective, the trade-off and debate between fuel, food and environment is not new to mankind. Already in the Mongolian empire during the 13th century, one had to choose between fuel for transport (feeding the 800 000 horses) and between food for the society [Liska and Heier 2013]. In any case, the most promising crops are represented by lignocellulosic species comprising willow, poplar and eucalyptus from forestry as well as miscanthus, switchgrass and sweet sorghum as perennial grasses [Russell 2009, Evans et al. 2010, Xie and Peng 2011]. Other crops that might be cultivated in smaller amounts are reed canary grass, giant reed, hemp, kenaf, and ethiopian mustard (a.k.a. Brassica Carinata) [Zegada-Lizarazu and Monti 2011]. Residues and waste represent a vast biomass feedstock that is available without increasing the cultivated land. The feedstocks are highly heterogeneous and stem from forestry, agriculture, municipalities, and industry. Depending on the location in the value chain, they can be classified as primary, secondary, or tertiary resource streams [Hoogwijk et al. 2003]. The residues are usually involved in a complex market and might be re-used throughout the life time in applications as e.g. fodder, fertilizer, soil conditioner, particle boards, and paper. The net availability is therefore somewhat difficult to predict. Overall, it is obvious that biomass is found in a vast variety of resource streams, and consequently, takes on different physical and chemical properties that will influence their behavior during utilization in different thermochemical energy conversion processes.
2.1.2 Fuel chemistry

Fuels are normally characterized by proximate and ultimate analysis as well as elemental ash composition [Vassilev et al. 2010]. The proximate analysis includes volatile matter, fixed carbon, moisture, and ash. The ultimate analysis includes carbon, oxygen, hydrogen, nitrogen, and sulfur. Table 1 presents proximate and ultimate analyses from a compilation of 86 different biomass fuels [Vassilev et al. 2010]. Based on those results it is clear that biomass is a heterogeneous fuel. In the same study, the elements in biomass were ranked in a decreasing order according to their abundance as follows: C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti. Biomass was also compared with coal and it was shown that biomass is highly enriched in Mn > K > P > Cl > Ca > (Mg, Na) > O > moisture > volatile matter and depleted in total ash, Al, C, Fe, N, S, Si, and Ti.

Table 1. Proximate and ultimate analyses of 86 different biomass fuels presented as weight percent. Revised from [Vassilev et al. 2010].

<table>
<thead>
<tr>
<th>Proximate (am)</th>
<th>Ultimate (daf)</th>
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<tr>
<td>VM (wt %)</td>
<td>C (wt %)</td>
</tr>
<tr>
<td>FC (wt %)</td>
<td>O (wt %)</td>
</tr>
<tr>
<td>M (wt %)</td>
<td>H (wt %)</td>
</tr>
<tr>
<td>A (wt %)</td>
<td>N (wt %)</td>
</tr>
<tr>
<td></td>
<td>S (wt %)</td>
</tr>
<tr>
<td>Mean</td>
<td>64.3</td>
</tr>
<tr>
<td>Minimum</td>
<td>30.4</td>
</tr>
<tr>
<td>Maximum</td>
<td>79.7</td>
</tr>
</tbody>
</table>

\(am = \text{as measured}; \ daf = \text{dry ash free basis}; \ VM = \text{Volatile Matter}; \ FC = \text{Fixed Carbon}; \ M = \text{Moisture}; \ A = \text{Ash content}; \ C = \text{Carbon}; \ O = \text{Oxygen}; \ H = \text{Hydrogen}; \ N = \text{Nitrogen}; \ S = \text{Sulfur}\)

The elemental ash composition has been characterized thoroughly during the years [Nordin 1994, Werkelin et al. 2005, Obernberger et al. 2006, Vassilev et al. 2010, Tao et al. 2012, Zevenhoven et al. 2012]. The most important ash forming elements with respect to ash transformation reactions have also been determined to include K, Na, Ca, Mg, Al, Si, P, S, and Cl [Boström et al. 2012]. Table 2 presents the composition of the most important ash forming elements for a wide variety of fuels including wood, grasses, straws, food processing residues, animal biomass, biomass mixtures, and contaminated biomass.
Table 2. Elemental ash composition (mmole/kg db) for 86 different biomass fuels. Revised from [Vassilev et al. 2010].

<table>
<thead>
<tr>
<th>mmole/kg db</th>
<th>K</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>3803</td>
<td>800</td>
<td>4506</td>
<td>1345</td>
<td>1081</td>
<td>4953</td>
<td>805</td>
<td>410</td>
<td>48</td>
</tr>
<tr>
<td>Minimum</td>
<td>34</td>
<td>29</td>
<td>173</td>
<td>47</td>
<td>20</td>
<td>3</td>
<td>28</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Maximum</td>
<td>13567</td>
<td>9623</td>
<td>14883</td>
<td>4022</td>
<td>10500</td>
<td>5768</td>
<td>1841</td>
<td>245</td>
<td></td>
</tr>
</tbody>
</table>

*db = dry bases*

The phase composition of the ash matter in biomass fuels do also influence the fuel conversion processes [Vassilev et al. 2013, 2014]. Data on phase composition determined mainly by XRD and light microscopy have been collected and it was found that the inorganic matter of biomass include mineral species, poorly crystallized mineraloids, as well as some amorphous phases [Vassilev et al. 2012]. Residues from dry water-soluble samples showed also that the water-soluble phases in biomass were chlorides, sulphates, oxalates, nitrates, carbonate, and amorphous material. The modes of occurrence of inorganic matter in biomass has also been investigated by selective leaching [Zevenhoven et al. 2012]. The results were additionally interpreted particularly for their influence on fluidized bed combustion. Samples from the following fuel classes were included: coal, peat, wood, agricultural wastes, and sewage sludge. For wood and agricultural fuels, it was found that the ash forming matter was mainly soluble and dominated by K, Ca, P and K, Cl, P for wood and agricultural fuels, respectively.

The chemical composition of biomass is heterogeneous, particularly with respect to the inorganic (ash) matter. Careful analyses by both elemental and phase composition are needed for a complete fuel characterization.

2.2 Combustion of solid biomass in fixed-beds

The first fixed-bed combustion unit mentioned in the literature dates back to 1874 when Albert Fryer patented a furnace in Nottingham. The furnace was named "the destructor" and the only purpose was to reduce the volume of waste material [Lewis 2007]. The most common type of biomass combustion technology of today is still the grate furnace and more than 350 units above 1 MWth were registered in Sweden in 2007 [Hermansson 2010]. The number of medium scale appliances (1-50 MW) within the EU is about 150 000 [MCP 2013]. Some benefits of this technology are related to the simplicity and robustness of operation. The material flows in the furnace may be arranged in co-current, counter-current, and cross-current mode depending
on the arrangement of fuel and air feeding. The most common arrangement seems to be the cross-current mode and implies that the fuel enters at one side of the furnace and the air is supplied perpendicularly to the fuel through the grate. The fuel is then transported and combusted on the grate and the residual ash is removed on the opposite side of the furnace. An illustration of two different grate burner size scales as well as a large scale power plant is presented in figure 3.

**Figure 3.** Pictures of small scale (40 kW) and large scale (60 MW) reciprocating grate burners and illustration of large scale grate fired power plant. The illustration (up, right) is adapted from [Yin et al. 2008] and the two pictures were taken by the author.
The mixing of fuel and air on the grate and the speed of fuel transport towards the ash removal system can be controlled by the use of a moving grate. For biomass combustion, the most typical configurations include reciprocating and vibrating grates, whereas the travelling grate is more common in coal combustion [Hermansson 2010]. Some other combustion control features for these types of grate furnaces are e.g. water cooling of the grate, speed and pattern of grate movements, location and dimensioning of air primary and secondary supply inlets, pre-heating of air, and flue-gas recycling to substitute parts of the air supply [Yin et al. 2008].

The grate combustion technology can also be described as a chemical reactor, and as such, the terms fixed-bed or packed-bed, are used. This reactor is differentiated from the fluidized bed and the entrained flow reactors used for suspension firing.

**2.3 Challenges in fixed-bed biomass combustion**

Until now, most grate furnaces have been designed for a specific fuel type which in the Nordic countries, implied process residues from forestry like saw mill operations as wood chips. However, a general increased usage of bioenergy, and particularly an increased utilization of high quality biomass resources such as clean wood in different business lines, has forced owners of grate furnaces to extend their feedstock base to include several different biomass fuels. Many of the "new" opportunity fuels that are supposed to substitute high quality wood fuels contain high amounts of nitrogen and ash forming elements that might cause an increase of gaseous and particulate emissions compared traditional wood fuels. In line with that, the operation stability of the combustion process, with respect to fuel efficiency, fuel bed disturbances, equipment wear, deposit formation (fouling and slagging), and corrosion, is affected by the physical and chemical properties of the fuel, with ash forming elements playing an important role. Figure 4 exemplifies phenomena such as slagging and fouling in biomass fired furnaces. In light of this, a review [Yin et al. 2008] pinpointed three key areas for research and development (R&D) for biomass based fixed-bed combustion technology that need progress, namely; i) control of pollutant emissions, ii) control of deposit formation and corrosion, and iii) development of mathematical models for design and troubleshooting of combustion processes.
2.4 Particle emissions in fixed-bed biomass combustion

2.4.1 Emission legislations

The European Commission has identified three focus areas that need more action towards the sustainability goals of 2020. One of those was to safeguard the Union's citizens towards environment-related pressures and risks to health and wellbeing [EU 7th EAP]. Based on this, a clean air program was announced in 2013 [EU Clean air]. Within this report, it was stated that, "urban air pollution is set to become the top environmental cause of mortality worldwide by 2050, ahead of dirty water and lack of sanitation." However, the announced clean air program is not only conducted to protect the health and wellbeing of the Union’s citizens, but also due to economic reasons since the total air pollution-related cost was estimated to 330-940 billion euro year 2010.

One efficient way to abate air pollution is to reduce emissions from areas that so far have been without legislation, for instance, small and medium scale combustion units. Two new legislations have been announced; the Ecodesign legislation that concerns small (<500 kW) appliances and the Medium Scale Combustion legislation that concerns appliances between 1 and 50 MW. The legislations are introduced from year 2020 (<0.5 MW), 2025 (>5 MW) and 2030 (<5 MW). The emission requirements are summarized in Table 3 and 4.
Table 3. Ecodesign requirements for automatically stoked boilers (20 - 500 kW) with emission limits for PM, NOx, CO, and OGC given as mg/Nm$^3$ at 0 °C, 101,3 kPa, dry gas and 10 % $O_2$. Revised from [Ecodesign 2014].

<table>
<thead>
<tr>
<th></th>
<th>PM (mg/Nm$^3$)</th>
<th>NOx (mg/Nm$^3$)</th>
<th>CO (mg/Nm$^3$)</th>
<th>OGC (mg/Nm$^3$)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 - 500 kW</td>
<td>40</td>
<td>200</td>
<td>500</td>
<td>20</td>
<td>77</td>
</tr>
</tbody>
</table>

Table 4. Medium Scale Combustion requirements (1-50 MW) with emission limits for PM, NOx, and SO$_2$ given as mg/Nm$^3$ at 0 °C, 101,3 kPa, dry gas and 10 % $O_2$. Data revised from [MCP 2013].

<table>
<thead>
<tr>
<th>Power (MW)</th>
<th>PM (mg/Nm$^3$)</th>
<th>NOx (mg/Nm$^3$)</th>
<th>SO$_2$ (mg/Nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing plants</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - 5</td>
<td>33</td>
<td>477</td>
<td>147</td>
</tr>
<tr>
<td>5 - 50</td>
<td>22</td>
<td>477</td>
<td>147</td>
</tr>
<tr>
<td>New plants</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - 5</td>
<td>18</td>
<td>220</td>
<td>147</td>
</tr>
<tr>
<td>5 - 50</td>
<td>15</td>
<td>220</td>
<td>147</td>
</tr>
<tr>
<td>Benchmark values</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - 5</td>
<td>7</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>5 - 50</td>
<td>4</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen in Table 3 and 4, there are five different types of emissions that are to be limited, i.e. particulate matter and four different gaseous pollutants. Products of incomplete combustion (PIC) in the flue gases are CO, organic gaseous carbon (OGC), tar, and soot particles (i.e. black carbon). These emissions can efficiently be reduced by thorough mixing of fuel/flue gases, long residence times within the gas phase (>1.5 s), high temperatures (>850°C), and by avoiding high excess oxygen levels [Obernberger et al. 2006]. Emissions of inorganic gases (e.g. NO$_x$ and SO$_2$) and ash particle matter (PM), originates from nutrients and ash forming matter in the fuels, and the abatement of these require other measures than those from incomplete combustion.

2.4.2 Particle formation and emissions

An efficient combustion process results in an aerosol where the fraction of unburned matter (soot and OGC) is in-significant and the aerosol is dominated by inorganic products. These products from fixed-bed combustion consists normally of two distinct size modes, i.e. fine and coarse, that in principal cover the whole aerosol particle size range from 0.002 to around 100 µm, as defined by [Hinds 1999]. In Figure 5, a schematic illustration of the typical particle mass size distribution of an ambient aerosol is shown.
Figure 5. Typical particle mass size distribution for an ambient aerosol. Adapted from [Lighty et al. 2011].

The primary (ultrafine) particles are formed through gas-to-particle processes, i.e. nucleation of gaseous species. Nucleation occurs when the partial pressure exceeds a critical saturation ratio, $S$, according to equation (1) where $p$ is the partial pressure of the gas and $p_s(T)$ is the saturation pressure at temperature $T$. A saturation ratio of 1 is sufficient for stable particle formation at a flat surface, but for particles where the curved surface slightly modifies the attractive forces between the molecules, a higher saturation ratio is required to reach the equilibrium state where the formation of a solid particle is stable. Lower saturation ratios cause evaporation of the particle. This phenomenon can be taken into account for pure substances by the Kelvin effect where surface tension, molecular weight, and density of the droplet liquid are considered. However, pure compounds are rare in real situations and effects of impurities and electric charge modify the situation greatly [Hinds 1999].

\[
S = \frac{p}{p_s(T)}
\]  

(1)

Generally, the nucleation in thermochemical conversion occurs by either cooling of the gas (by e.g. secondary air jets), or the formation of new gas species (by e.g. oxidation) with lower vapor pressures. The nucleated compounds will thereafter grow by coagulation and/or surface deposition.
Surface deposition means that volatilized gas species distribute on the surfaces of existing nucleated particles by condensation and chemical reactions. Coagulation means that particles collide with one another due to the relative motion between them and adhere to form larger particles. The coarse mode constitutes larger particles entrained from the fuel bed as solid particles, consisting of either inorganic mineral grains or unburned char residues. In fresh (primary) biomass combustion emissions, the particle size distribution does, obviously, not include a mode of “secondary” aerosols, and the mass size distribution can instead be described more clearly as comprising a fine mode of particles below 1 µm (PM$_1$) and a coarse mode >1 µm [Sippula 2010, Wiinikka 2005, Boman 2005]. Depending on combustion efficiency, the fine mode may include both unburned carbonaceous particles as well as inorganic particles. A conceptual model of three fine (<1 µm) particle classes from fresh biomass combustion emissions were proposed; i.e. organic dominated particles, soot agglomerates and alkali particles [Kocbach-Bolling et al. 2009]. At the same time, the formation pathways and typical particle mass size distributions of biomass combustion aerosols were summarized by [Sippula 2010]. Figure 6 presents an illustration of the formation routes for the different types of fine aerosol particles as well as the coarse fraction.
Fig. 6. Illustration of the particle formation in biomass combustion. Adapted from [Sippula 2010].

Parts of the particles are deposited inside the furnace, boiler, and flue gas channel depending on their e.g. size and gas flow conditions. With the aid of computational fluid dynamic (CFD) simulations it is however possible to reduce the coarse emissions by avoiding high velocity streams that could carry particles away from the grate. The existence of the typical two-mode size distribution as discussed above was illustrated in an experimental study where PM emissions from four different grate furnaces were determined by size, separating the particles before and after particle removal devices [Sippula et al. 2009]. The results were adapted and presented in figure 7.
Figure 7. Particle mass size distribution before particle filtration devices measured at four different small grate-fired heat plants. Adapted from [Sippula et al. 2009].

The elemental compositions of the coarse particles usually contain refractory elements like Ca, Si, and Mg, but smaller amounts of volatile elements have also been found [Brunner 2006]. The traces of e.g. K in the coarse mode might derive from entrainment of solid mineral impurities as feldspars, without volatilization, which also is supported by a numerical study [Jokiniemi et al. 1994] finding that condensation of volatile alkali species on coarse ash particles are not favored. However, according to [Brunner 2006] the existence of other volatile elements like S, Cl, Zn, and Pb, might be explained by condensation upon coarse ash particles. The composition of the fine inorganic particles in biomass combustion has been shown to contain the elements K, Na, S, Cl, Zn, Pb, O, C, and P. In most cases for most biomass fuels, the composition is dominated by K, S, Cl, and O in the form of KCl and K$_2$SO$_4$ [Boman 2005, Wiinikka 2005]. The fine particles from wood fuels have also been shown to contain smaller amounts of Na and Zn. In one study K$_3$NaSO$_4$ was additionally identified by XRD and was a probable host compound for Na, while the Zn-speciation was not possible to identify [Boman et al. 2004]. Other studies have indicated the presence of Zn as small nucleus of ZnO particles [Torvela et al. 2014]. The combustion of waste wood fuels has been shown to result in elevated concentrations of Zn and Pb in the fine particles, as shown in experiments with fluidized bed boilers [Enestam et al. 2011, 2013]. Some combustion experiments with agricultural fuels have also shown that phosphorus can be found in the fine
particles [Wiinikka et al. 2007, Tissari et al. 2008, Bäfver et al. 2009]. For oat combustion in particular, XRD analyses identified KPO$_3$ and KH$_2$PO$_4$ in the fine particles during fixed-bed combustion [Boström et al. 2009]. The presence of C in the fine PM during efficient combustion is most probably related to alkali carbonates, e.g. K$_2$CO$_3$.

The group of the six elements - K, Na, S, Cl, Zn, and Pb - is in the literature often referred to as “volatile” elements. A clarification to this point is that the elements themselves should not be considered volatile. It is rather the speciation of the formed compounds that have high vapor pressures at combustion temperatures, and are therefore, volatilized from the fuel bed. This phenomenon, i.e. release of ash forming elements, has gained increased attention in the biomass combustion research lately owing to its impact on fine particle emissions, deposit formation and high temperature corrosion.

\section*{2.4.3 Methods for reduction of particle emissions}

PM emissions from combustion sources can be reduced by three principally different methodological measures; i) "pre-process" cleaning, ii) "in-process" cleaning, and iii) "post-process" cleaning. The first measure, pre-process cleaning, means that impurities are removed from the fuel prior to combustion and is more common for coal fuels where larger particles can be removed according to the actual particle weight or even molecular weight in more advanced technologies. The term “beneficiation” has been used by the mining industry for similar purposes. For biomass, pre-process cleaning by washing has been suggested and tested with promising results [Jenkins et al. 1996]. The working principles are based on removing water-soluble compounds, containing e.g. K, Cl, and S. It is however a rather messy procedure and requires both additional drying and control of waste water drainage. Washing is therefore not applied to any larger extent. However, experiments with a delayed harvest for grass crops, i.e. when the crops are left over-wintering in the field, has been demonstrated to reduce the alkali content compared to the fresh harvest [Burvall 1997]. Another kind of pre-process cleaning would be careful harvesting and handling of biomass to avoid inclusion of soil particles that might be harmful to both PM emissions and operational stability. These are routines that are easy to implement and are mostly followed by the heat and power production industry. The second category, in-process cleaning (also denoted primary measures), have so far been implemented to some extent to cope with certain problems, e.g. the abatement of SO$_2$ emissions. The abatement of PM emissions has not yet been implemented by the industry to the same extent, although some initiatives have been undertaken. However, the scientific data available is rather comprehensive and the knowledge in this field is in many aspects
ready for further development and implementation. Altogether it can be concluded that fine inorganic PM emissions can be reduced by primary “in-process” measures through capture of certain elements like K, Na, and Zn; where K is the most critical one for biomass fuels. The third measure, post-process cleaning (also denoted secondary measures), is the most commonly implemented methodology applied for PM emission control. The coarse PM fractions are removed by standard cyclones and are today used on heat and power plants from some few MW and upwards, owing to the robust and simple construction. Fine PM can also be removed by the use of electrostatic precipitators (ESP) and bag house filters. Still, such devices have so far not been commercially available (or motivated) for combustion facilities below about 10 MW [VTT 2006]. However, the development in this field is rapid regarding smaller and more cost-effective solutions, owing to the more stringent coming legislation on PM emissions.

2.5 Deposit formation in fixed-bed biomass combustion

2.5.1 Deposit formation on heat transfer surfaces (fouling)

One of the most studied and understood technical operational problems within the field of combustion are probably deposit formation and corrosion on heat transfer surfaces. A detailed description of deposit formation in biomass combustion systems, including the underlying sub-processes can be found in the extensive literature within the field [Frandsen 2010, Broström 2010, Frandsen 2005, Kaufmann et al. 2000, Bryers 1996]. Deposit formation is not restricted to any particular combustion technology and it is therefore possible to generalize parts of the results and apply them in both fixed-bed, fluidized bed, and entrained flow reactors. There are of course technology specific aspects related to temperature, fluid dynamics, residence time, etc. that need to be considered, but in general deposit formation can be described as a four stage process. These include: i) release of ash forming matter from the fuel, ii) aerosol formation, iii) transport of ash forming species to the surface of the heat exchanger, and iv) build-up and shedding of deposits. Deposit formation is therefore, in accordance with the formation of fine particles emissions, initiated and controlled by the release of ash forming elements. However, there are of course aerosol transformation processes like coagulation, fragmentation, sulfation of alkali chlorides, etc. that affect the aerosol properties in terms of size distribution, morphology and viscosity, which in turn might affect the actual deposition onto the surfaces. Entrainment of coarse particles also affect deposit formation. The boundary conditions around the deposit surfaces should also be accounted for. CFD models that consider such processes have been developed [Yin et al. 2008 and references therein, Leppänen et al. 2014] and some of them
include the fate of coarse particles due to entrainment from the fuel bed. But, even though extensive research has been performed, there is a need for more generalized models [Weber et al. 2013, Yin et al. 2008]. Most of the models are adapted as post-processors in CFD domains where boundary conditions supply the free board with inlet conditions such as temperature and velocity, as well as concentration and speciation of compounds [Yin et al. 2008]. Dedicated ash-release studies are therefore needed to supply proper information to the post-processor model.

### 2.5.2 Slag formation on the grate (slagging)

Slag formation is an operational problem that causes combustion instabilities due to the plugging of fuel feeding, air supply, and ash flows on a grate (figure 4). The severity of slag formation in real-scale combustion units could be measured by the frequency of error alarms caused by changes of the operation parameters as e.g. temperatures and oxygen concentration. The worst case is complete shutdown of the process for manual removal of the slag. The underlying phenomenon (physical and chemical sub-processes) of slag formation on grates is not as well understood and described as some other ash related operational issues, e.g. deposit formation on heat transfer surfaces or agglomeration in fluidized beds. It is also of a rather specific character since different grate burner configurations show different sensitivity to slag formation [Ashmelt 2015]. This is probably due to different temperature profiles in the fuel bed and different temperatures of surrounding surfaces, but also the mechanical robustness with removal of slag particles from the grate and down into the ash feeding screw. However, even if the slag particles are removed from the grate, large particle sizes could cause plugging in the ash removing system. Therefore, it is important to understand slag formation, both mechanisms initiating the slag formation and the mechanisms that are involved in the growth of particles. Further, it is probable that the "stickiness" of slag particles affect the severity of slag formation. Combining all these parameters (fuel, process control, and grate configuration) would be crucial if slag formation on the grate were to be described in a more generalized predictive model.

Rather extensive research efforts have been performed relating to slag formation, mainly focusing on the elucidation of the ash chemical aspects. Already in the beginning of the 20th century, it was concluded that pyrite (FeS$_2$) was responsible for the formation of glass due to dissolution of Fe-components into the silicate ash matter normally found in coals. And even before that - in 1895 - research had been published where the melting temperature of slag was linked to the proportional distribution of basic and acidic components in the slag [Bryers 1996]. More recently, for fixed-bed
biomass combustion, evaluations of slag formation severities have been performed by measuring the sintering degree and the slag fraction. The size of slag particles has occasionally been determined as a third assessment method. The research so far has shown that the slag formation properties are affected by both total ash content and fuel ash chemical composition [Öhman et al. 2004a]. SEM-EDS analysis of cross sections of slag particles have revealed that the elemental composition comprises mainly K, Ca, and Si, but also smaller amounts of Na, Mg, and Al [Gilbe et al. 2008]. In the same study, it was concluded that the Si-content, both inherent and via contaminations, influenced slag formation through reactions with alkali compounds, eventually leading to the formation of sticky molten alkali-silicate particles. It was also discussed that these particles remained in the residual ash and initiated the slag formation. Increasing the Ca-content of the system, either by co-combustion with other fuels or by applying additives, has been shown to reduce slag formation [Öhman et al. 2004b, Wang et al. 2011]. However, it is not fully understood whether the Ca compounds quench the initial K-Si melt formation through incorporation of Ca, or if the anti-slagging benefits owe to the direct formation of solid and thermally stable Ca-silicates that reduce the amount of Si available for the formation of the low-temperature melting K-silicates.

The framework for understanding slag formation on the grate during fixed-bed biomass combustion has been established. However, critical knowledge is still missing related to the initial melt formation, properties of the melts (e.g. viscosity), and the subsequent growth of slag particles, especially when combining external conditions as physical and dynamical properties of the grate.

2.6 Release of ash forming elements in fixed-bed biomass combustion

2.6.1 Definition of release

The term “release” is hereafter used for describing the volatilization of gaseous compounds from a fuel particle or fuel bed during thermochemical conversion. It was previously stated that the volatile elements of relevance comprise K, Na, S, Cl, and Zn since they form compounds with high vapor pressures at combustion conditions and parts of these species form fine particles upon cooling of the flue gas. Thus, by combining release data and concentration of the respective ash forming elements, it is possible to evaluate the level of PM emissions and the deposit formation potential. Fuels with high concentrations and high release values of K and Na give rise to situations where deposit formation and high PM emissions are expected. It is
therefore desirable to reduce the release of the alkali elements in order to improve the combustibility for such fuels. This is achieved by capturing the alkalis on the residual ash of the grate in the form of slag and/or non-sintered bottom ash. It has been shown that even though smaller amounts of slag can be handled, most of the alkali elements should preferably be captured in non-sintering bottom ash to enable smooth process operation. For biomass applications, a number of classes of compounds are of relevance, including chlorides, carbonates, sulfates, silicates, alumina silicates, and phosphates. The thermal stability of these compounds varies greatly depending on specific composition and combustion temperature. Hence, attempts to reduce the release of ash forming elements must be assessed together with the risk of slag formation to reach a compromise between the risks with deposit formation on heat exchanger surfaces and fine PM emissions, as well as the risks of slag formation on the grate. This is possible through the aid of “fuel engineering”.

2.6.2 Principles of fuel engineering

*Fuel engineering* was first mentioned (according to Web of Science) back in 1948 regarding boiler installations within the pulp and paper industry. The popularity of the term seems to have decreased within the traditional thermochemical fuel conversion areas, and is nowadays mostly used by the nuclear power industry. Within the bioenergy industry today, the term "fuel design" is more often used. While fuel design focuses more specifically on the properties of the fuel, the term fuel engineering can be considered as the combined approach of both fuel design and combustion control. In this context, fuel engineering can be described as the development of generalized and applicable tools for prediction and mitigation of critical ash and emission related issues in certain applications. These ash chemical tools should be based on a fundamental understanding of the underlying mechanisms combined with technological process specific considerations.

The term fuel design specifically within this work is a methodology where fuel mixtures are viewed by their molar concentration (mole/kg) of major ash forming elements to facilitate rough estimations of ash transformation reactions during the thermochemical conversion. As discussed by [Boström et al. 2012] the most significant ash forming elements in biomass are K, Na, Ca, Mg, Al, Si, P, S, and Cl. In addition, Zn can be added to this list as the most prominent trace metal in biomass that is enriched in the fine PM. As outlined in the conceptual model presented in [Boström et al. 2012], the route of ash transformation may, for the case of simplification, be divided into primary and secondary reactions.
The primary reactions denote the affinity of the ash forming elements to oxygen in relation to the carbon-hydrogen matrix. This gives vital information about the volatility of elements. A schematic description of the secondary reactions is facilitated by dividing the products from the primary reactions into basic and acidic reactants, as illustrated in figure 8. The compounds are arranged according to reactivity (most reactive on top) based on thermodynamical considerations, i.e. pure equilibrium conditions. Thus, for fuel compositions where there is a competition for P among the base cations, primarily K-phosphates will form first. If K is consumed, the turn then comes to Na, etc. In a reversed case, if there is a competition for K among the acid components, primarily K-phosphate will form. If P is consumed, the turn comes to S, etc. This is however a simplification, and further reactions will take place in real situations where mixed compounds, such as e.g. K-Ca-silicates may form due to even lower free energy levels for such systems.

Based on these principles, it is possible to describe the order in which the ash forming compounds are consumed. When combined with molar concentrations, it is even possible to estimate which compounds that ought to dominate the respective ash fractions. However, in real situations, the presence of mixed phases (solutions) and restrictions related to specific formation mechanisms may change the final outcome. Some of the mechanistic restrictions might be handled by considering and describing the properties of the reactants in ash transformations. In an attempt to cope with this, the concept of the so-called Lewis acid-base system was applied by [Skoglund 2014], on ash transformation reactions in biomass thermal conversion processes, to develop the description model of the underlying chemical phenomenon. The working principles are based on structural chemistry and describe atoms and molecules in terms of electron donors (Lewis base) and electron acceptors (Lewis acid). In primary ash transformations, i.e. the formation of oxides/hydroxides, all elements act as acids whereas oxygen acts as a base to form $\text{O}^-$ and $\text{OH}^-$. In secondary ash transformation, where oxides and hydroxides are already formed, the oxygen atom in compounds like KOH and CaO act as Lewis bases whereas the non-oxygen atom in compounds like $\text{SiO}_2$ and $\text{SO}_2$ act as Lewis acids. The products from secondary ash transformation reactions are instrumental for further reaction paths in thermochemical energy conversion. At this stage, the elements K, Na, Ca, Mg, Al are considered to have formed Lewis acids (positively charged ions) whereas the elements Si, P, S, Cl are present as Lewis bases (negatively charged ions, molecular or atomic). Tertiary ash transformations proceed by using products from secondary reactions as reactants together with other products either from secondary or primary reactions. These tertiary reactions may take place in several steps, where the
molecular Lewis bases formed by Si, P, and S, can act as both bases and acids due to the dual character of the molecular ions (e.g. SiO$_3^{2-}$).

Throughout this work, chemical thermodynamics was applied with the fuel design principles where the fuel composition is viewed according to the molar concentration. The mechanistic approach with Lewis acids and bases was used as a foundation for the understanding of the basic inorganic chemistry. When the base is set by the fuel design, it should be combined with process control to gain knowledge about temperatures, gas concentrations, and flow conditions inside a particular combustion unit. Overall, the combination of fuel design and combustion control enables the assessment of alkali volatility and the slag formation potential of the capturing phases, which is in focus for different fuel engineering situations, to support the introduction of new ash rich biomass resources for utilization in heat and power production.

**Figure 8.** Primary products of ash-forming elements from the initial stages of combustion could be divided into two categories, basic and acidic compounds. Adapted from [Boström et al. 2012].

<table>
<thead>
<tr>
<th>basic compounds</th>
<th>acidic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH(l,g) (K$_2$O)</td>
<td>P$_2$O$_5$(g)</td>
</tr>
<tr>
<td>NaOH(l,g) (Na$_2$O)</td>
<td>SO$_2$(g)/SO$_3$(g)</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>SiO$_2$(s)</td>
</tr>
<tr>
<td>MgO(s)</td>
<td>HCl(g) (Cl$_2$)</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>CO$_2$(g)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O(g)</td>
</tr>
</tbody>
</table>

### 2.6.3 Aspects of release and capture of potassium – state of the art

**Underlying parameters**

The parameters influencing the release of alkali elements during thermochemical conversion of biomass has been studied throughout the years by several different research groups in an array of different apparatuses. It was concluded that the fuel chemical composition and temperature are the most vital parameters for alkali release [Baxter et al. 1998]. The understanding of alkali release made progress in the mid 90's.
owing to experiments performed in bench-scale batch-operated reactors by the research group at the Danish Technical University [e.g., Knudsen et al. 2004, van Lith et al. 2006]. With the bench-scale experiments, it was possible to isolate the influencing parameters and elucidate the effects of temperature, reducing/oxidizing conditions, and the role of Cl and Si on alkali release, especially for wood and straw fuels. Regarding the fuel chemical composition, it was observed that Cl increased the release of alkali, whereas Si decreased the release. However, one important conclusion based on the results from these studies was also that the results from bench-scale release studies should be carefully interpreted when compared and used for predictions in real-scale boilers [Frandsen 2010]. It was observed that the alkali release from bench-scale reactors was occasionally higher than in real-scale reactors, possibly owing to different sample sizes and kinetic restrictions with e.g. silicate formation. More recently, the release has also been studied by the research group of University of Eastern Finland where it was shown that sulfur addition decreased the potassium release for different chlorine concentrations [Sippula et al. 2008]. Another research group performed bench-scale experiments with clay kaolin as additive to determine the capturing potential of alkali elements [Tran et al. 2004ab, 2005]. The experiments showed that kaolin captures different potassium species in both reducing and oxidizing conditions. Similar studies for coal fuels have also been performed [Punjak 1988]. Overall, the pioneering studies mentioned here laid a large foundation to the present understanding of alkali release mechanisms and the possible abatement methods.

Influence of combustion control

A number of fuel engineering attempts have been performed with the aim of reducing the alkali release during grate combustion of biomass. A custom-designed 10 kW updraft combustion reactor was, for example, constructed to determine the effect of air staging on particle emissions and it was shown that PM$_1$ and the release of the alkali elements decreased about 50% for both wood and bark pellets [Wiinikka and Gebart 2005]. The effect of air staging was believed to be linked to a lower fuel particle temperature since the oxygen concentration around burning fuel particles is connected to its temperature during the char conversion. The approach of air staging for alkali release control was also used in a full-scale 7 MW gasification boiler firing forest residue. The K release in this unit was clearly lower than in a typical rotating grate boiler [Sippula et al. 2009]. It should be noted that the fuels were not similar in the two boilers, but according to previously mentioned ratios of K/Cl and K/Si, the release potential was estimated to be even greater in the gasification unit. Despite the unfavorable fuel chemical composition, the release was low for the gasification unit. The fuel bed
temperature was not measured in this experiment either. The same research group made another effort to study the effect of air staging on PM$_1$ emissions by using a top-feed pellet burner with two different air staging settings [Lamberg et al. 2011]. The K release was also reduced by approximately 50% during operation with the lowest primary lambda compared to pre-defined factory settings of the burner. Accordingly, the literature suggests that air staging can be applied to reduce K release and there seems to be consistency regarding the governing mechanism, i.e. a reduced fuel bed temperature. Empirical data on fuel bed temperatures are unfortunately lacking from these studies. Another process related method with the same aim - to reduce alkali release - was recently suggested within the ERA-NET project FutureBioTec [Futurebiotec 2012]. However, this method is based on the opposite principle regarding primary air supply; it was shown that PM$_1$ emissions were reduced when the volume flow through the bed increased. It was discussed that this effect was due to a higher cooling effect of the total primary air flow applied. However, no scientifically published results that support this phenomenon have been found.

Kaolin addition

Kaolin is a clay mineral composed mainly of the mineral kaolinite, Al$_2$Si$_2$O$_5$(OH)$_4$. The mineral kaolinite undergoes three important transformations upon heating. Firstly, it dehydrates above 450°C leading to the formation of amorphous metakaolinite [Bellotto et al. 1995, Ptacek et al. 2011] according to the endothermic reaction in equation (2). Secondly, the metakaolinite reacts with gaseous K-compounds (here exemplified with KCl even though other compounds are possible) according to the reactions in equations (3 and 4). It is believed that the reaction starts with physisorption and thereafter proceeds with chemisorption [Tran et al. 2005]. Thirdly, if no interactions with cation forming constituents occur, metakaolinite will crystallize into cristobalite and mullite above 1100°C [Silva et al. 2011].

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (s) \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 (s) + 2\text{H}_2\text{O} (g) \qquad (2)
\]

\[
\text{Al}_2\text{Si}_2\text{O}_7(s) + 2\text{KCl}(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{KAlSiO}_4(s) + 2\text{HCl}(g) \qquad (3)
\]

\[
\text{Al}_2\text{Si}_2\text{O}_7(s) + 2\text{SiO}_2(s) + 2\text{KCl}(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{KAlSi}_2\text{O}_6(s) + 2\text{HCl}(g) \qquad (4)
\]

A review of the scientific literature showed that few studies have focused on determining the K release during fixed-bed combustion of biomass with kaolin as fuel additive. In fact, only one study was found, and that was for oat and wood combustion in a horizontal fed 20 kW pellet boiler [Tissari et al. 2008]. The experiments showed that K release was reduced for oat while it
was increased for wood. Some similar studies have been performed, although focusing on the fine (ash) PM emissions, during kaolin addition. In one study, oat grains were combusted with three levels of kaolin in a 20 kW pellet burner and it was shown that the PM$_1$ emissions decreased by 31% and 57% for the two kaolin addition levels [Bäfver et al. 2009]. Another study showed that the particle emissions can be reduced for wood fuels (pine bark and tree thinnings) when used in a 20 kW underfed pellet boiler [Boman et al. 2008]. The role of kaolin in deposit formation has also been studied, and combustion experiments with demolition wood in a custom-designed reactor showed that kaolin addition shifted the Cl-fractionation so that it was mostly found in the flue gas, and not in the PM fraction [Khalil et al. 2012]. Based on this, it was discussed that the corrosion potential decreased upon kaolin addition. It was further shown in a pilot-scale experiment with a 150 kW reciprocating grate boiler that addition of kaolin to empty fruit bunch enabled the surface temperature of a deposition probe to remain high for a longer time than for the case without kaolin [Madhiyanon et al. 2013]. A conclusive remark for all these five studies is that the residual ash was not analyzed to determine the capturing mechanisms and phases of K even though it was discussed, based on literature data, that chemisorption with alumina silicates were most probably responsible for the positive effects.

The capturing mechanisms of alkali have been studied in more detail by authors focusing on slag formation. An experimental study was performed to show how addition of kaolin influences the slagging tendency for a problem free (stem wood) and a problematic (contaminated stem wood) wood fuel [Öhman et al. 2004b]. It was seen that kaolin decreased the slagging somewhat for the problematic fuel, but increased it dramatically for the problem free fuel. The main conclusion for the increased slagging was linked to the formation of low-temperature melting Ca-Al-K silicates. Another study investigated the influence of kaolin on the slagging tendency for corn stover in a 50 kW underfed pellet burner [Xiong et al. 2008]. They found that kaolin addition increased the concentration of KAlSi$_2$O$_6$ clearly in both the slag and the non-sintered ash. A similar experimental set-up was used for studying combustion of oat grains mixed with kaolin [Boström et al. 2009]. Several different ash fractions were characterized and it was seen that the fine PM emissions were reduced and potassium was captured in the phases KAlSiO$_4$ and KAlSi$_2$O$_6$ in the non-sintered bottom ash. In general, the main effects of the ash transformation were attributed to the formation of the two high melting point compounds KAlSiO$_4$ and KAlSi$_2$O$_6$. However, ashing experiments in a bench-scale furnace showed that the ashes from eight different agricultural fuels mixed with kaolin also contained other phases such as KAl$_3$Si$_5$O$_{11}$, KAlSi$_3$O$_6$, KAl$_2$(Si$_3$Al)O$_{10}$(OH)$_2$, Na$_{1.3}$K$_{0.7}$Si$_2$O$_5$, illite, and
amorphous material [Steenari et al. 2009]. Hence, ash transformations within the $K_2O-\text{Al}_2O_3-\text{SiO}_2$ system are complex.

Wrapping up the performed fuel engineering attempts with kaolin addition concludes that kaolin seems to decrease fine particle and deposit forming matter in parallel with reducing slag formation. However, complete mass balances and determinations of the total K release are rare. In addition, it seems like the studies focusing on PM emissions lack close up analyses of the actual K capturing phases in the residual ash. Further, accurate control of fuel bed temperatures is rare, especially with respect to the mineral transformations of metakaolinite. Studies in entrained flow reactors have actually shown that the alkali capturing potential of kaolin decreases at the high temperatures in these kind of reactors (>1400°C) [Mwabe et al. 1996]. As a final comment related to previous work on the use of kaolin as additive, it should be stressed that the research so far has not been focused on finding optimum addition levels for different fuels and thermochemical conversion applications, nor has techno-economic or ecological aspects been fully evaluated.

**Co-combustion with peat**

As an alternative to adding certain chemicals or minerals to a biomass fuel, the use of co-combustion between different fuels may be applied. As such, peat has been used in co-combustion rather extensively in Sweden and Finland by the heat and power industry to improve the combustibility of wood fuels. One important aspect of peat in co-combustion scenarios is that peat has shown to be a very heterogeneous fuel as illustrated in figure 9. [Pommer et al. 2009]. In that study, eight different peat fuel samples were chosen to represent the variation in Swedish peat types based on the concentrations of Ca, Al, Si, and S. The eight peat types were then co-combusted with forest residues to determine the influence of peat ash composition on agglomeration temperature in a fluidized bed reactor. It was shown that all peat types increased the agglomeration temperature compared to the reference case with pure forest residues, but it was also shown that the different peat types resulted in different agglomeration temperatures. Other studies have shown that peat increases the agglomeration temperature [Lundholm et al. 2005, McDonnell et al. 2010]. Peat co-combustion has also shown positive effects on deposit formation and high temperature corrosion [Theis et al. 2006, Kassman et al. 2011]. However, scarce information is available focusing on fixed-bed combustion, especially concerning the effects of the peat ash heterogeneity on the ash chemical behavior. One study, however, was recently published where it was shown how PM1 emissions vary between different wood-peat admixtures in a
residential pellet boiler [Lamberg et al. 2013]. One of the conclusive remarks was that peat shows good possibilities to be used as an additive for fuels with "medium-high" K contents in order to control the PM₁₀ emissions. It was also noted that the current understanding of peat co-combustion is too low and more work is needed. Another experimental study characterized the aerosol from co-combustion of demolition wood and peat ash in a laboratory fixed-bed reactor and found that K volatilization was decreased with peat ash addition [Backman 2013].

![Figure 9. Variation of ash forming elements in 83 different peat samples. Adapted from [Pommer et al. 2009]](image)

**Summary of release aspects**

Owing to extensive research efforts on the fundamentals of ash transformations, we have reached a rather solid understanding of the basic ash related operational issues and fine particle emissions during thermochemical conversion. A number of fuel engineering attempts have also been performed with positive results. There is however a need for more accurate determinations of the ash release, especially for dedicated fuel engineering situations in order to measure, validate, and develop the models for prediction of ash related problems and particle emissions. In particular, for the development of mathematical models, more information is needed related to the temporal release of ash forming matter, *i.e.* a description of the...
ash transformation reactions and phenomena "along" the dynamic fuel conversion processes.
3. Materials and methods

3.1 Fuels and additives

Eleven different fuel assortments and two additives were used in this work. All fuels, including mixtures of peat and additives, were combusted in pelletized form. The main ash forming elements analyzed by ICP-MS/AES for the studied fuels and the kaolin additive are presented in Table 5. The kaolin additive was supplied by Thiele Nordic AB as a powder with a particle size below 2 µm and with a phase composition consisting of 100 % kaolinite. The ammonium sulfate additive was supplied from VWR Chemicals as crystals (>99.5 %) and grind coarsely before blending with the biomass.

Table 5. Ash content (wt % db) and elemental ash composition (mmole/kg db) of the eleven fuels and kaolin additive used in this work.

<table>
<thead>
<tr>
<th></th>
<th>SW1</th>
<th>SW2</th>
<th>EW</th>
<th>FR</th>
<th>S</th>
<th>WS1</th>
<th>WS2</th>
<th>WS3</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>Kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>0.40</td>
<td>0.40</td>
<td>0.7</td>
<td>2.4</td>
<td>2.1</td>
<td>5.7</td>
<td>4.48</td>
<td>9.0</td>
<td>6.3</td>
<td>4.0</td>
<td>10.4</td>
<td>n.a.</td>
</tr>
<tr>
<td>K</td>
<td>14.4</td>
<td>13.9</td>
<td>20.4</td>
<td>43.5</td>
<td>63.9</td>
<td>320</td>
<td>178</td>
<td>373</td>
<td>12.8</td>
<td>2.6</td>
<td>20.5</td>
<td>21.9</td>
</tr>
<tr>
<td>Na</td>
<td>1.0</td>
<td>0.7</td>
<td>0.2</td>
<td>6.1</td>
<td>4.8</td>
<td>13.0</td>
<td>8.7</td>
<td>9.3</td>
<td>8.7</td>
<td>4.3</td>
<td>13.0</td>
<td>73.1</td>
</tr>
<tr>
<td>Ca</td>
<td>18.7</td>
<td>20.5</td>
<td>52.9</td>
<td>125</td>
<td>125</td>
<td>100</td>
<td>75.1</td>
<td>128</td>
<td>185</td>
<td>97.3</td>
<td>115</td>
<td>3.3</td>
</tr>
<tr>
<td>Mg</td>
<td>5.8</td>
<td>9.3</td>
<td>9.4</td>
<td>24.7</td>
<td>18.1</td>
<td>41.1</td>
<td>28.3</td>
<td>46.5</td>
<td>28.8</td>
<td>20.6</td>
<td>28.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe</td>
<td>n.a.</td>
<td>0.7</td>
<td>0.4</td>
<td>4.3</td>
<td>1.8</td>
<td>0.9</td>
<td>n.a.</td>
<td>9.8</td>
<td>89.5</td>
<td>124</td>
<td>136</td>
<td>n.a.</td>
</tr>
<tr>
<td>Al</td>
<td>1.3</td>
<td>1.9</td>
<td>1.1</td>
<td>13.3</td>
<td>6.3</td>
<td>22.2</td>
<td>8.0</td>
<td>26.0</td>
<td>70.4</td>
<td>96.4</td>
<td>126</td>
<td>8270</td>
</tr>
<tr>
<td>Si</td>
<td>15.0</td>
<td>6.5</td>
<td>1.5</td>
<td>100</td>
<td>30.6</td>
<td>285</td>
<td>395</td>
<td>787</td>
<td>502</td>
<td>160</td>
<td>1160</td>
<td>7260</td>
</tr>
<tr>
<td>P</td>
<td>1.4</td>
<td>2.0</td>
<td>3.3</td>
<td>14.9</td>
<td>19.0</td>
<td>42.0</td>
<td>12.4</td>
<td>28.5</td>
<td>9.7</td>
<td>12.9</td>
<td>22.6</td>
<td>7.2</td>
</tr>
<tr>
<td>S</td>
<td>2.2</td>
<td>1.8</td>
<td>2.7</td>
<td>12.5</td>
<td>12.5</td>
<td>59.3</td>
<td>28.5</td>
<td>43.3</td>
<td>159</td>
<td>81.1</td>
<td>68.6</td>
<td>13.3</td>
</tr>
<tr>
<td>Cl</td>
<td>1.7</td>
<td>0.8</td>
<td>2.0</td>
<td>&lt;2.8</td>
<td>&lt;2.8</td>
<td>73.3</td>
<td>64.9</td>
<td>99.0</td>
<td>8.5</td>
<td>0.0</td>
<td>14.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Zn</td>
<td>0.2</td>
<td>0.2</td>
<td>0.5</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.1</td>
<td>0.4</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.2</td>
</tr>
</tbody>
</table>

n.a. = not analyzed; SW = Soft wood; EW = Energy wood; FR = Forest residues; S = Salix; WS = Wheat straw; P = Peat

The most dominating ash forming elements for biomass in general are K, Ca, and Si. This was also the situation for the studied fuels in this thesis, except for the peat fuels, which are generally low in K, while Al and Fe are elevated. A compositional triangle in this ash chemical system can therefore be used to show how the fuels spread out in this system with the most important elements. The elements Na and Mg were also included since the behavior of these are similar to the ones of K and Ca, respectively. Thus, figure 10 displays the compositional triangle of the system K₂O (+Na₂O) - CaO (+MgO) - SiO₂ and shows how the fuels in Table 5 are distributed within this system. It is seen that the wood fuels (EW, SW1, SW2, S, FR) gather quite far away from the SiO₂-corner with rather high fractions of the CaO-component.
Another group is formed by the wheat straw fuels that are dominated by K$_2$O and SiO$_2$ in varying proportions. The last group consists of the peat types that are found along the SiO$_2$ and CaO line but heavily dominated by SiO$_2$. Included in the same diagram were also the liquidus isotherms of the ternary phase diagram K$_2$O - CaO - SiO$_2$ in order to assess the melting properties of the different fuels. The further away from the red lines, the lower the risk for ash melting. However, the risk for extensive volatilization of K-compounds increases simultaneously since the amount of capturing Si-compounds are reduced, especially for compositions close to the K$_2$O-corner when the CaO-component is also low. The application of this tool is demonstrated in the results section.

**Figure 10.** Compositional triangle (weight percent) for the system K$_2$O (+Na$_2$O) - CaO (+MgO) - SiO$_2$ displaying the relative concentration of the components for the eleven fuels that were used in experiments throughout this work. Liquidus isotherms adopted from [Morey et al. 1930] for the ternary phase diagram K$_2$O - CaO - SiO$_2$. 
3.2 Combustion reactors

Three different reactors were used throughout this work to perform combustion experiments. The first one, the single pellet reactor, was used to study details of the ash transformations on a single pellet level. The method enabled accurate mass balance closures and the ability to follow the combustion with respect to the two fuel conversion stages, i.e. devolatilization and char combustion. However, it was only possible to analyze the residual ash, and no measurements of gases or particulate matter were performed. It was also restricted to batch-wise operation. The second reactor, the residential pellet boiler, is a typical market-relevant set-up used in the national testing and certification P-marking system and by some research groups for combustion experiments. The set-up was used to study the ash transformations during continuous fuel feeding with focuses on slag formation and fine particle emissions. Another important feature was that it was possible to study all ash fractions, i.e. combining results from both residual ash and the aerosol phase. The third reactor, the grate reactor, was used similarly as the pellet boiler, but also with the aim to simulate fuel conversion in medium scale grate boilers used for local district heating and in some applications for combined heat and power production. The features of the grate made it possible to control the combustion process in more detail. The different features of these three reactors complemented each other well and proved to comprise a valuable chain of tools for fuel engineering experiments.

3.2.1 Single pellet reactor

The single pellet reactor was constructed in-house and consisted of an electrically heated furnace with internal dimensions measuring 200 x 130 x 130 mm. Oxidizing gas was supplied through a grate at the bottom of the furnace and the sample holder was hung from an analytical balance (1 mg resolution) at the top of the reactor. The reactor was used in batch wise operation. The heated furnace was separated from a quenching tower that was situated above the furnace separated by a slide hatch to enable quenching with N₂ gas. An inspection window on the front door was used to monitor the combustion processes. A schematic illustration is presented in figure 11. The reactor was described in more detailed in paper III, and also used in paper IV and V.
Figure 11. Schematic illustration and picture of the single pellet reactor. The picture was taken by the author.

3.2.2 Residential pellet boiler

The residential pellet burner was manufactured by EcoTech and had a nominal effect of 20 kW. Pellets are fed from beneath by a fuel feeding screw and is pushed upwards to the rim where the ash is removed from the burner down onto the boiler floor. The burner is supplied with primary air through slits on the grate and secondary air through the nozzle above the fuel bed, as marked in figure 12. The fuel feed is regulated intermittently, i.e. the screw operates at constant speed, but half the time at 50 % load. The outer rim of the burner turns clockwise simultaneously with the fuel feeding screw to remove the ash from the burner. The burner was installed in a reference boiler that is used in Sweden for national certification tests for residential pellet burners. The set-up was used in Paper I, II and IV.
Figure 12. Residential pellet burner docked into a reference boiler. The pictures are taken by the author.

### 3.2.3 Grate reactor

The reactor consists of a commercially available (Ariterm Multijet 40 kW) burner and tailor made primary and secondary combustion chambers. It is a typical grate furnace with such features as cross-current operation and reciprocating grate rods. The fuel feeding was supplied continuously by regulating the rotation speed of the screw. Primary air was supplied through the grate rods and secondary air was supplied through slits in the construction frame. Pre-heaters were used to heat the incoming primary air. The set-up is illustrated in figure 13 and described in more detail in paper VI, the single paper where this set-up was used in this thesis.

Figure 13. Grate reactor set-up (left) and grate burner with reciprocating rods (right). The pictures are taken by the author.
3.3 Ash sampling and flue gas measurement

The ash compounds are fractioned within the combustion unit to end up as three streams; i) residual ash on the grate, ii) particulate matter in the aerosol phase, and iii) gaseous compounds in the aerosol phase. Obtaining a complete description of the combustion process requires collection of all three streams. It should be mentioned that fraction ii) and iii) may deposit in the combustion unit and influence the mass balance closures. Previous studies have shown that, in grate boilers, most of the total ash (70–95 wt-%) is found on the grate [Frandsen 2010]. The value for K specifically varies, but needs to be collected from both the residual ash and the particulate phase. When the collection of particles is conducted downstream of the heat exchanger, i.e. in colder parts (<200°C) of the flue gas system, all K compounds have formed condensed particles and there is thus no need for collection of gaseous K compounds. The release of K can be determined by two different approaches, either via the residual ash or via the particulate matter. Both approaches derive from mass balances and weight concentrations of the respective ash forming elements, according to equations (1) and (2).

\[
\text{Release (\%)} = \left(1 - \frac{m_{\text{ash}} c_{\text{ash}}}{m_{\text{fuel}} c_{\text{fuel}}} \right) \cdot 100
\]  

\[
\text{Release (\%)} = \left(\frac{m_{\text{PM1}} c_{\text{PM1}}}{m_{\text{fuel}} c_{\text{fuel}}} \right) \cdot 100
\]

\( m_{\text{ash}} = \) mass of residual ash collected after the experiment (kg)
\( c_{\text{ash}} = \) concentration of residual ash forming element, EDS or ICP-MS/AES (wt-% or mg/kg)
\( m_{\text{fuel}} = \) mass of fuel used during the experiment (kg)
\( c_{\text{fuel}} = \) concentration of ash forming element from ICP-MS/AES (mg/kg)

These two approaches are associated with different aspects and may give dissimilar results, which also have been discussed by [Brunner 2006]. The first approach that is based on the residual ash determines what is released from the fuel bed, whereas the other approach based on PM1 determines the fraction of the released matter that is found in the flue gas channel. Thus, the difference between these two constitutes losses within the combustion unit, i.e. deposit formation. There are, however, practical aspects of the issue, and these have to do with mass balances. Collection of a representative amount of residual ash is challenging during short combustion experiments or when using fuels with low ash contents. The collection of PM1, if sampling is performed correctly, gives a more accurate mass balance during typical combustion experiments performed in laboratory scale. The drawback is of
course that the results reflect not only the ash transformations occurring on the grate, but additionally aspects of deposit formation. Another aspect that should be mentioned is related to the analytical methods. ICP-MS/AES is a well known method that gives more accurate results than the EDS, especially for heterogeneous ash fractions as the residual ash of grate boilers. However, the homogeneous speciation and size distribution of the PM\textsubscript{1} samples enables the use of EDS, and consequently, it has been applied for determinations of the concentration of ash forming elements in the PM\textsubscript{1}. In the following, the collection of the three ash fractions is described.

### 3.3.1 Combustion gases

A Fourier Transformed Infrared (FTIR) instrument (Gasmet DX4000) was used (paper I, IV, VI) to measure combustion gases by determining the concentrations of CO, CO\textsubscript{2}, H\textsubscript{2}O, NO, SO\textsubscript{2}, HCl, and O\textsubscript{2} (by an oxygen sensor). The data was used to continuously follow the burnout efficiency and for compensations and normalizations of emission values.

### 3.3.2 Flue gas particles

Two different methods were used to sample flue gas particles, traditional filters and impactor sampling. The filter method (paper VI), based on iso-kinetic principles in Swedish standards SS028426, collects both fine and coarse particles on glass fiber or quartz filters and is normally used for information of total suspended particulate matter denoted TSP or as used here, PM\textsubscript{tot}. The impactor method, based on the classical cascade impactor principle [Marple and Willeke 1976] was used in papers I, IV, and VI, and collects particles by inertial impaction, designed to separate particles into different size classes according to aerodynamic particle diameter. (The aerodynamic diameter of an irregular particle is defined as the diameter of the spherical particle with a density of 1000 kg/m\textsuperscript{3} and the same settling velocity as the irregular particle [Hinds 1999]). The Dekati low pressure impactor (DLPI) [Marjamäki \textit{et al.} 2000] was used, which separates particles into 13 stages ranging from 0.030 to 10 µm and in this work un-greased aluminum foils were used as collection substrates. The size separation enabled chemical and morphological analysis of the fine and coarse mode separately. The impactor measurements were also used to determine PM\textsubscript{tot}. The flue gas temperature at the collection point was below condensation temperature for all K-compounds and the sampling was performed iso-kinetically for a correct representation of the particle size distribution.
3.3.3 Residual ash

The residual ashes formed during combustion experiments in the residential pellet boiler and the grate reactor were collected, weighed, and sieved to separate slag particles from the non-sintered bottom ash. Particles caught above a 3.15 mm sieve were classified as slag. The slag fraction was assessed visually and by hand to determine the sintering degree. The procedure was developed by [Öhman et al. 2006] and later revised in two steps [Lindström et al. 2007 and Diaz-Ramirez et al. 2012], presently defined as a five degree classification where degree 1 define non-sintered bottom ash and degree 4/5 define fully sintered ash. The latest revised classification is presented in Table 6.

Table 6. Description of sintering degree for slag collected from the residual ash. Adapted from [Diaz-Ramirez et al. 2012].

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Non sintered ash residue, i.e. no fused ash (clear grain structure)</td>
</tr>
<tr>
<td>2a</td>
<td>Partly sintered ash, i.e. particles contained clearly fused ash that breaks at a light touch (distinguishable grain structure).</td>
</tr>
<tr>
<td>2b</td>
<td>Partly sintered ash, i.e. particles contained clearly fused ash that holds together at a light touch but is easily broken apart by hand (distinguishable grain structure).</td>
</tr>
<tr>
<td>3</td>
<td>(Totally) sintered ash, i.e. the deposited ash was fused to smaller blocks that still are breakable by hand (slightly distinguishable grain structure).</td>
</tr>
<tr>
<td>4</td>
<td>Totally sintered ash, i.e. the deposited ash was totally fused to larger blocks that not are possible to break by hand (no distinguishable grain structure).</td>
</tr>
</tbody>
</table>

3.4 Chemical characterization of fuel and ash

The collection of fuel samples was conducted carefully to decrease risks of contaminations and to achieve representative samples. The standards for sample collection (Swedish Standard 18 71 13) and sample preparation (Swedish Standard 18 71 14) were used as a support in the sample handling.

The collected residual ash and aerosol particle samples were subjected to subsequent chemical analysis for three types of information: elemental composition (EDS and ICP-MS/AES), phase composition (XRD), and morphology (SEM). The SEM-EDS was usually used as a first assessment of the samples. The ICP method is considered a more accurate method with much lower detection limits than EDS, used for determination of the elemental composition. Both these methods are typically used in this kind of combustion research. The XRD method though, is not as commonly used in this field, but was used in all papers to supply data on the phase
composition. The combined use of these methods has proved to be highly valuable for the research within high temperature inorganic chemistry.

3.4.1 Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)

The ash fractions were analyzed (paper I, II, III, IV, and VI) for morphology and elemental composition with a Philips XL30 Environmental Scanning Electron Microscopy (ESEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS). The SEM applies an electron beam instead of electromagnetic radiation, as in light microscopy, to obtain high-resolution images of small samples. EDS is a method to determine the elemental composition by measuring the energy level and number of X-ray photons that are formed when a sample is subjected to the electron beam. The energy levels of the X-ray photons are unique for all atoms and this feature enables determination of the elemental composition of the sample. The residual ash samples were grinded in an agate mortar and/or crushed in a ball mill to homogenize the samples before attachment to the sample holder consisting of an aluminum stub covered with carbon tape. Preparation of particulate matter samples were not necessary and therefore attached straight onto the sample holder. Fine particulate samples were usually analyzed directly onto the aluminum foils, whereas coarse particles were put onto carbon tape. All analyses were performed at TEC-lab, Umeå University by the author.

3.4.2 Inductively coupled plasma (ICP-MS/AES)

Inductively coupled plasma analysis was used in papers II, III, IV, V, and VI to determine the elemental composition of ash fractions. The method gives similar data as EDS, but with a higher accuracy and sensitivity, especially for heterogeneous samples such as residual ash [Baernthaler et al. 2006]. The methodology for ICP analysis include preparation by grinding, dissolution of solid samples, ionization of the solution with inductive coupled plasma (ICP), and identification of elements with atomic emissions spectroscopy (AES) or mass spectrometry (MS). The dissolution is an important step, and it should result in a fully homogeneous solution without solid residues for the analysis to fully represent the solid sample. A multi-step pressurized microwave assisted methodology with HNO₃/HCl/HF was applied.

3.4.3 Powder X-ray diffraction (XRD)

The ash samples were, in all papers, analyzed with powder X-ray diffraction for information about the phase composition. Crystal structures can be identified by the diffraction pattern formed by the scattering of X-rays upon
hitting planes within the crystal. The instrument consisted of a Bruker d8Advance X-ray diffractometer, a primary Göbel mirror and a Väntec-1 detector. The diffractometer was set in θ-θ mode and continuous scans with Cu Kα radiation were applied at an angle rate of 1°/min. The Bruker software and PDF-database were primarily applied to make initial phase identification. Besides identification of crystalline structures (qualitative measurements), the Rietveld technique was used to semi-quantitatively determine the amount of identified phases by the use of crystal structure data from the ICSD database. The samples were prepared by grinding and then mounting them in plastic holders (large samples) or silicon low-background holder (small samples).

3.5 Thermodynamic equilibrium calculations

The route of gaining knowledge in science may be described as an iterative process between empirical data collection and the formulation of models. Models are formulated with different degrees of sophistication and can be based on both hard facts ("laws of nature") and on soft facts (empirical correlations). Within the research field of combustion, computer aided models have been developed and applied to simulate thermochemical processes in order to understand phenomena and develop processes [Kaer et al. 2006, Weber et al. 2013, Leppänen et al. 2014]. The research presented in this work applied mathematical models for chemical thermodynamics to simulate fixed-bed combustion processes and particularly issues with slag and deposit formation as well as fine particle emissions.

The commercial software FactSage [Bale et al. 2002, 2009] was used throughout this work to calculate phase equilibria and thermodynamic properties for multi-phase and multicomponent systems. FactSage was introduced in 2001 through the fusion of FACT-win and ChemSage and it consists of four different software categories, although with the core related to the databases and calculations. The database contains thermodynamic data for both pure compounds and for non-ideal solution phases that are vital for high temperature inorganic chemistry, primarily in combustion, mainly due to the ordering of components within oxide slags. Within the calculation category of FactSage, the “equilib module” is considered the workhorse and it calculates the concentration of chemical compounds when specified reactants reach phase equilibria under certain system constraints. These constraints are defined in three steps as model inputs by; i) defining reactants, ii) selecting possible compound and solution products, and iii) setting the final conditions, i.e. temperature and pressure within the system. Based on this information, the software finally calculates the phase equilibria, i.e. the set of products that results in the lowest possible Gibbs
energy. The routine of Gibbs energy minimization is based on the algorithm and thermochemical functions of ChemSage [Eriksson and Hack 1990].

Third party users have been able to adopt the Gibbs energy minimization routine of FactSage, named ChemApp, and programmed new interfaces that are beneficial in applied engineering. One such software used in this work was ChemSheet [Koukkari 2009]. It was first developed by VTT in 1999 and it incorporates the thermodynamic library of ChemApp into Microsoft Excel as an add-in. This union creates a thermochemical simulation tool that combines the flexibility and practicality of spreadsheet operations with rigorous multi-phase thermodynamic calculations that has proven useful in applied engineering. In the following, short descriptions on how thermodynamic equilibrium calculations were used in the different papers of relevance are given.

In paper III, calculations were performed to determine proper addition levels of kaolin to soft wood and wheat straw. This was performed by calculating the fraction of gas phase potassium at different addition levels of silicon and aluminum. In papers V and VI, calculations were performed to support the evaluation and interpretation of the experimental results. The focus in the analysis of the calculation results were on the distribution of potassium within the condensed phases at different assumed process conditions, especially the K-distribution between silicates and carbonates.

There are several restrictions to phase equilibria calculations that need to be considered. Firstly, kinetic limitations and imperfect mixing, i.e. the calculations do not account for time of reaction or mixing of system components. Additionally, "activation energy barriers" that might be present in certain reactions are not accounted for. It should be mentioned that ChemSheet enables the use of immaterial constraints (constrained Gibbs energy method) that can be used to deal with work effects to describe e.g. reactions kinetics or surface energies. These features were not applied in this thesis. Another restriction to phase equilibria calculations is the potential lack of data. For example, within the phosphate system of relevance for some biomass fuels, several pure compounds as well as solutions with silicates are missing. There are also systems that are poorly evaluated and optimized, e.g. the addition of K₂O and Na₂O to the fully optimized six-component system CaO-MgO-Al₂O₃-FeO-Fe₂O₃-SiO₂ in the FT-Oxid database. Since this is a vital chemical system with respect to ash transformation in thermal conversion of biomass, the results from phase equilibria calculations should be interpreted carefully. The databases are constantly being developed and future updates will probably incorporate these optimized data. The choice of solution model is also a delicate task when simulating ash transformation.
processes and potassium transformation in particular. Thus, prior to the selection of a particular set of databases and solution models, an extensive amount of screening calculations were performed to evaluate the effect of different solution models for the investigated problems. With a combination of adequate input data, calculation methodology, and interpretation procedures, the thermodynamic equilibrium calculations serve as a valuable tool when evaluating experimental results and when predicting operational problems in thermochemical energy conversion processes.
4. Summary of results from included papers

4.1 Biomass and peat co-combustion

The objective with paper I was to determine the influence of peat ash composition on particle emissions and slag formation in grate biomass co-combustion.

Three different peat types were co-pelletized with forest residues (15 wt-% peat), Salix (15 wt-% peat) and wheat straw (40 wt-% peat). The fuel blends and the pure biomass fuels (12 fuels in total) were combusted in a residential pellet burner (figure 12). The particle mass concentration emissions were measured using a 13-stage low-pressure impactor and analyzed by SEM−EDS for information about the elemental composition. The release of potassium was calculated based on fine particle measurements and SEM-EDS analyses. The residual ash was collected and characterized after the experiments to determine slag fraction and the sintering degree. The main results are presented in figure 14 and shows how the K-release and the slag fraction varies with the peat type.

![Figure 14](image-url)

**Figure 14.** Relation between K release (staples) and slag formation (squares/lines). K release was calculated from K found in fine particles (PM1), and slag formation was calculated from the amount of formed slag and ash content in fuel. FR, forest residues; WS, wheat straw; S, Salix; P1-P3, different peat types.
The conclusions were summarized as follows:

- Co-combustion with all peat types reduced fine particle emissions.

- Potassium in the residual ash was found in the slag fraction and/or in the non-sintered bottom ash as $K_2SO_4$, $K_3Na(SO_4)_2$, KCl, KAlSiO$_4$, KAlSi$_3$O$_8$.

- There are clear differences between the peat types regarding their ability to influence fine particle emissions and slag formation.

- A high ratio of Al/Si increases the possibility of forming solid and thermally stable K–Al silicates that can more easily be removed with the ash-feeding system.

- A high ratio of Ca/Si reduces the risk of severe slag formation.

- The most suitable peat type for biomass co-combustion is a non-contaminated (i.e. ~4% ash) peat with high Al/Si and Ca/Si ratios and sulfur present as a reactive mineral.

- The blending proportion of peat may be defined on an individual basis for each co-combustion scenario with respect to the ash-melting properties within the compositional triangle $(K_2O + Na_2O) - (CaO + MgO) - (SiO_2)$.

### 4.2 Slagging in fixed-bed combustion

The objective of paper II was to perform a comprehensive synthesis to determine critical ash-forming processes and compositions in fixed-bed combustion generalized for phosphorus-poor biomass fuels.

This was done by a systematic review of data and experiences gathered from combustion experiments with 36 different biomasses conducted in a residential pellet burner (figure 12). The data comprises information of elemental and phase composition, sintering degree, and slag fraction of the formed bottom ashes and slags. Furthermore, the viscosity of the slags were predicted by using several different models.

The main results are presented in figure 15.
Figure 15. Ternary compositional diagrams (wt %) for the K2O (+ Na2O) − CaO (+ MgO) − SiO2 system: (A) visual sintering category (the colors represent the four graded visual classifications of the formed slag: purple, category 1; blue, category 2; dark green, category 3; and dark gray, category 4); (B) slag fraction (the color of the numbers represent the fraction of fuel ash that forms slag (expressed in units of wt %): green, < 10 wt % (no tendency to form slag); yellow/green, 11 −30 wt % (minor tendency); orange, 31 −50 wt % (moderate tendency); red, 51 −70 wt % (moderate/major tendency); and black, > 70 wt % (major tendency)); (C) bottom ash; and (D) molten ash. Each number represents a fuel presented in Table 1 (paper II). The liquidus isotherms are adopted from the K2O − CaO − SiO2 system reported in the work of [Morey] while the composition in the triangle was calculated by also including Mg and Na. The numbers in the diagrams shown in panels (A) and (B) represent the fuel ash composition, while the numbers in the diagrams shown in panels (C) and (D) represent the bottom ash and molten ash compositions, respectively.

The conclusion from this work was that the melt fraction and the viscosity of the molten ash are critical for the slag formation processes. It was also found that the fuels could be classified into four groups according to their slagging tendency as presented below.
- **No slag.** This group consists of fuels low in K and Si and high in Ca, as e.g. non-contaminated stem wood. These fuels will not form silicate melts but it is possible that salt melts are formed during combustion. The viscosity of those melts is however low and they should not cause any slagging issues in the burner.

- **Minor slagging tendency.** This group consists of fuels with somewhat elevated Si concentrations compared to the previous group. Examples of such fuels are bark, logging residues, and slightly contaminated stem wood. A minor fraction of silicate melt is formed but the viscosity is high enough not to cause sticking of ash particles.

- **Moderate slagging tendency.** This group consists of fuels with an even further increased Si content and comprise contaminated wood fuels and straws and grasses with high Ca contents. The ash consists of a higher melt fraction and the viscosity is lower than the previous group and thus more sticky.

- **Major slagging fuels.** This group consists of fuels dominated by K and Si as different kind of straw and grass fuels and results in extensive formation of molten ash.

### 4.3 Alkali transformation in single pellet combustion

The objective with **paper III** was to determine the temporal release of ash forming elements during single pellet combustion of soft wood and wheat straw. This was achieved by collecting the residual ashes formed during the experiments after the devolatilization phase and after the char conversion phase. A macro-TGA was used as an experimental set-up to study the ash transformations. Wet chemical analysis were conducted on the fuels and ashes to determine the release of ash forming elements. The results are presented in figure 16.
Figure 16. Release of ash forming elements from single pellet combustion of soft wood (upper) and wheat straw (lower) in the Macro-TGA at 700°C (left) and 1000°C (right), presented as mean values from three replicates with standard deviation for both devolatilization and full conversion. Na values for wood were below -200 % due to methodological errors.

The four main conclusions were summarized as follows.

- The total K release was around 30 % and 20 % for wood and straw respectively, which is typical for such fuels during grate combustion. The furnace temperature was however not seen to influence the total release significantly. The explanation to this is probably that the actual fuel conversion temperature was rather high in both cases and the availability of silicon for both fuels, as quartz contamination for wood and as amorphous silica for straw.

- The temporal release behavior was however shown to be both temperature and fuel dependent. For wood, the release of K occurred mainly during char combustion. A similar behavior was observed for...
straw at 700°C, but at 1000°C the majority of K was released during the devolatilization. The differences are presumably explained by different phase composition as wood-K was considered to reside as amorphous matter whereas straw-K was considered to reside as alkali salts.

- The phase composition of the residual ashes was heterogeneous as four different phases were identified; crystalline compounds, molten ash (glass), char, and amorphous non-glass compounds. K was mainly captured by amorphous non-glass compounds for wood, and by molten ash (glass) for straw.

- The release of Na in the straw experiments was considerably higher than the release of K. It was discussed that differences in reduction potential of K and Na could affect secondary capture within the residual ash while the alkali species are transformed upon heating. It was also discussed that differences in silicate formation between the two alkali counterparts might explain the observed differences. No conclusive explanations were however presented.

The findings from the present work gave insight into the specific alkali behavior during biomass fuel conversion.

### 4.4 Kaolin additive in single pellet biomass combustion

The two biomass fuels soft wood and wheat straw were shown in paper III to exhibit different characteristics regarding K transformation during fuel conversion. The objective of paper IV was therefore to study the influence of kaolin addition on the release of ash forming elements and on the formation of residual ash for soft wood and wheat straw. Combustion experiments were performed single pelle-wise in a macro-TG reactor at three furnace temperatures and three kaolin addition levels as well as a reference case without kaolin. The single pellet results were compared with results from a continuously fed pellet boiler. The main results are presented in figure 17.
Figure 17. Release of K determined from single pellet combustion of soft wood-kaolin and wheat straw-kaolin admixtures at different temperatures (700/850/1000°C) and four kaolin addition levels presented as mean values from three replicates with accompanying standard deviation for both devolatilization (bright staples) and char combustion (dark staples). Four single pellet devolatilization experiments were performed. The release from the pellet boiler is represented as black lines.

The conclusions are summarized as follows.

- The release of both refractory elements (i.e. Ca, Mg, Al, Si, P) and volatile elements (i.e. K, Na, Cl, S, Zn) during single pellet combustion were generally in agreement with the release behavior during combustion in the pellet boiler.

- Kaolin captured K equally efficiently for both fuels despite differences in speciation within the two fuels.

- The optimum kaolin addition level to both fuels was found to be the medium level, i.e. 1 and 4 wt % for wood and straw, respectively. The low addition reduced the release slightly but not entirely as the medium level. The high level was therefore unnecessary in terms of alkali release. Excessive addition might also increase the entrainment of coarse particles and puts stress on the ash feeding system.

- The two high temperature melting compounds KAlSiO$_4$ and KAlSi$_2$O$_6$ were identified in the straw ashes and are considered the major capturing phases of K. For wood however, only trace amounts of KAlSi$_2$O$_6$ was identified in the residual ash. And since no other K containing phases were identified, K seemed to be captured in amorphous non-glass compounds in both experimental set-ups.
Kaolin addition resulted in less slag formation for wheat straw especially but the residual ashes from both pellet boiler experiments was more porous in the case with kaolin than without kaolin.

The outcomes of this work might be used as support in future fuel engineering situations and the application of kaolin as an additive for alkali control.

4.5 Temporal release and phase transformation

The twin objective of paper V was to; i) determine the semi time-resolved release of K, S, and Cl for two different biomass fuels (energy wood and wheat straw) by off-line residual ash analysis, and ii) to determine the phase composition in the residual ash to enable a discussion regarding the K-release mechanisms. Combustion experiments were performed single pellet wise in a macro-TGA reactor. Samples were collected by quenching the fuel conversion process at nine subsequent occasions during the fuel conversion. The main results are presented in figure 18 and Table 7.

![Figure 18. Release of volatile ash forming elements from single pellet combustion of wood in the macro-TGA at 850°C, presented as mean values from three replicates.](image-url)
Table 7. Phase composition of energy wood and wheat straw char/ashes from macro-TGA experiments at 850°C. The samples were analyzed with P-XRD and presented as weight percent of the crystalline fraction.

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The conclusions are summarized as follows:

- The semi time-resolved release behavior differed between wood and straw.

- The K-release for wood started halfway through the char combustion stage and 50 % was released at full conversion. The K-release for straw occurred in two steps, ~10 % during devolatilization and then an additional ~10 % early in the char combustion, thus 20 % at full conversion.

- The residual ash for wood was low in crystalline phases and the majority of K resided as amorphous (non-molten) matter. It was discussed that "char-K" could be a host phase for K from which the release occurs. Release through decomposition of K-carbonates was not considered likely.
• The residual ash for straw contained more crystalline K-compounds but the most of K was captured as amorphous (molten silicates) matter. The K-release behavior was similar to the one of Cl and it was concluded that K-release from straw can be described as evaportaiion of KCl.

• More research with other experimental techniques are needed to study this further to support the development of K-release models from different fuels.

4.6 Control strategies for reduction of alkali release

The objective with paper VI was to explore primary control strategies for reduction of the release of K, Na, and Zn from the fuel bed during grate combustion of woody biomass, by determination of the influence of both process parameters and fuel additives on the ash transformation in general and the release behavior of alkali and zinc in particular. A matrix of six experiments were performed in a grate reactor (figure 13) by using the pure fuel and two different additives (kaolin and ammonium sulfate), all three fuels combusted co-pelletized with burner settings (process parameters) that result in a "cold" and a "hot" case in terms of fuel bed temperature. Fine particles were collected with a low pressure impactor and the residual ash was collected after the experiments. The samples were characterized by ICP-MS/AES, SEM-EDS and P-XRD for a thorough evaluation of the ash transformations. The main result comprised of release values as presented in figure 19 and phase composition of the residual ash presented in Table 8.

![Figure 19](image)

**Figure 19.** The release of K, Na, and Zn calculated from the elemental concentration (ICP-AES) in fine particles.
Table 8. Phase composition (XRD) of the bottom ash from the six experiments presented as weight percent of the crystalline fraction.

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W_C = Wood Cold; W_H = Wood Hot; W_K_C = Wood Kaolin Cold; W_K_H = Wood Kaolin Hot; W_AS_C = Wood Ammonium Sulfate Cold; W_AS_H = Wood Ammonium Sulfate Hot

The conclusions are summarized as follows:

- The deposit formation process in future small-scale biomass CHP plants can be significantly reduced by controlling the release of the major deposit forming ash species.

- Correct settings of the process parameters have a significant potential to reduce the release even without the use of additives.

- Such correct setting seems to be related to a low fuel bed temperature, here achieved by a high fuel bed lambda, which caused a cooling effect by the excess air.
• The use of additives reduced the release of both alkali and Zn even further, especially when using kaolin but also for the application with ammonium sulfate.

• For the kaolin case, the release reduction of K was linked to the formation of KAlSiO$_4$ in the bottom ash while the formation of K$_2$SO$_4$ can explain the release reduction when using ammonium sulfate.

• A good control of the fuel bed temperature is important when kaolin is applied in fuel engineering situations to avoid a de-activation of the metakaolinite.

• The Ca-content of the biomass should be considered in parallel with the K-content when the additivation levels of kaolin are calculated due to the formation of Ca/Al-silicates.
5. Aspects of fuel engineering

5.1 Fine particle emissions during fixed-bed combustion

This chapter compiles all the PM emissions and K-release data from the papers and compares those with the proposed PM emission legislations to assess the potential for fuel engineering to act as a measure for the mitigation of PM emissions. The data is presented in Table 9. The legislation limitations for PM emissions were set to 40, 33, and 22 mg/m$^3$ ($O^\circ C$, 101.3 kPa, dry gas, 10% $O_2$) for existing boilers at different plant sizes (Table 3 and 4). Note that the legislation concerns $PM_{tot}$ whereas the data in Table 9 shows $PM_1$.

The only pure fuel that showed $PM_1$ emissions below the limitation was clean stem wood of softwood. However, when used in the grate reactor, one of the soft wood fuels exceeded the limitation. With the use of kaolin though, it was possible to reduce the PM emissions significantly, but it was also shown that the combustion needed to be controlled carefully in order to avoid high fuel bed temperatures and subsequent "de-activation" of the capturing properties of kaolin. It is reasonable to believe that combustion of pure wood pellets with ash contents around 0.3 per cent can be used without fuel engineering efforts or post-process PM cleaning technologies, despite the legislation.

The combustion of all the other fuels included in this work are expected to require measures for PM emission reduction. The logging residues and peat co-combustion experiments showed that peats 2 and 3 reduced the PM emissions significantly and it might be possible that no post-process PM cleaning is necessary. The PM emissions for Salix exceeded the legislation limitation during peat co-combustion, but the K-release of 6-10 % indicates that further reductions are possible. Thus, it is possible that a more optimized fuel engineering effort could decrease the need of post-process PM cleaning.

The results also indicate that for fixed-bed combustion of wheat straw, not only fuel engineering measures are enough, but also post-process cleaning technologies are most likely needed. The best peat co-combustion scenario reduced the PM emissions by about 50 % but that was not enough for the legislation. However, the combustion experiments with kaolin showed better potential to reduce the PM emissions and only a few per cent of the K-content was released. Since wheat straw is such a K-rich fuel, small variations in the release might affect the $PM_1$ emissions substantially. A calculation with the most K-rich wheat straw (#3) showed that if only
chlorides are assumed to form, the K-release must not exceed 1.0 % if emissions are not to exceed a limit of 33 mg/m³.

The overall conclusion concerning fuel engineering is that the expected high PM emissions from certain ash rich biomass fuels can be efficiently mitigated by fuel engineering. Thus, this should be applied alone or in parallel with traditional PM cleaning technologies.

Table 9. PM₁ emissions and K release data from measurements in this thesis. The PM₁ emissions are normalized to mg/m³ at 0°C, 101.3 kPa, dry gas, 10 % O₂.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Additive</th>
<th>Temperature</th>
<th>PM₁ (mg/m³)</th>
<th>Release (wt-%)</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft wood 2</td>
<td>-</td>
<td>low</td>
<td>38</td>
<td>17</td>
<td>VI</td>
</tr>
<tr>
<td>Soft wood 2</td>
<td>-</td>
<td>high</td>
<td>54</td>
<td>29</td>
<td>VI</td>
</tr>
<tr>
<td>Soft wood 2</td>
<td>kaolin 1 %</td>
<td>low</td>
<td>16</td>
<td>7</td>
<td>VI</td>
</tr>
<tr>
<td>Soft wood 2</td>
<td>kaolin 1 %</td>
<td>high</td>
<td>27</td>
<td>13</td>
<td>VI</td>
</tr>
<tr>
<td>Soft wood 2</td>
<td>Am sulf</td>
<td>low</td>
<td>23</td>
<td>14</td>
<td>VI</td>
</tr>
<tr>
<td>Soft wood 2</td>
<td>Am sulf</td>
<td>high</td>
<td>30</td>
<td>17</td>
<td>VI</td>
</tr>
<tr>
<td>Soft wood 1</td>
<td>-</td>
<td>-</td>
<td>21</td>
<td>17</td>
<td>IV</td>
</tr>
<tr>
<td>Soft wood 1</td>
<td>kaolin 3 %</td>
<td>-</td>
<td>3</td>
<td>1</td>
<td>IV</td>
</tr>
<tr>
<td>Soft wood 1</td>
<td>-</td>
<td>low</td>
<td>n.a.</td>
<td>30</td>
<td>IV</td>
</tr>
<tr>
<td>Soft wood 1</td>
<td>-</td>
<td>high</td>
<td>n.a.</td>
<td>33</td>
<td>IV</td>
</tr>
<tr>
<td>Soft wood 1</td>
<td>kaolin 1 %</td>
<td>low</td>
<td>n.a.</td>
<td>1</td>
<td>IV</td>
</tr>
<tr>
<td>Soft wood 1</td>
<td>kaolin 1 %</td>
<td>high</td>
<td>n.a.</td>
<td>5</td>
<td>IV</td>
</tr>
<tr>
<td>Wheat straw 2</td>
<td>-</td>
<td>-</td>
<td>271</td>
<td>16</td>
<td>IV</td>
</tr>
<tr>
<td>Wheat straw 2</td>
<td>kaolin 7 %</td>
<td>-</td>
<td>22</td>
<td>1</td>
<td>IV</td>
</tr>
<tr>
<td>Wheat straw 2</td>
<td>-</td>
<td>low</td>
<td>n.a.</td>
<td>18</td>
<td>IV</td>
</tr>
<tr>
<td>Wheat straw 2</td>
<td>kaolin 4 %</td>
<td>high</td>
<td>n.a.</td>
<td>22</td>
<td>IV</td>
</tr>
<tr>
<td>Wheat straw 2</td>
<td>kaolin 4 %</td>
<td>low</td>
<td>n.a.</td>
<td>2</td>
<td>IV</td>
</tr>
<tr>
<td>Wheat straw 2</td>
<td>kaolin 4 %</td>
<td>high</td>
<td>n.a.</td>
<td>3</td>
<td>IV</td>
</tr>
<tr>
<td>Logging residues</td>
<td>Peat 1, 15 %</td>
<td>-</td>
<td>68</td>
<td>7</td>
<td>I</td>
</tr>
<tr>
<td>Logging residues</td>
<td>Peat 2, 15 %</td>
<td>-</td>
<td>25</td>
<td>3</td>
<td>I</td>
</tr>
<tr>
<td>Logging residues</td>
<td>Peat 3, 15 %</td>
<td>-</td>
<td>32</td>
<td>3</td>
<td>I</td>
</tr>
<tr>
<td>Salix</td>
<td>Peat 1, 15 %</td>
<td>-</td>
<td>86</td>
<td>8</td>
<td>I</td>
</tr>
<tr>
<td>Salix</td>
<td>Peat 2, 15 %</td>
<td>-</td>
<td>83</td>
<td>10</td>
<td>I</td>
</tr>
<tr>
<td>Salix</td>
<td>Peat 3, 15 %</td>
<td>-</td>
<td>59</td>
<td>6</td>
<td>I</td>
</tr>
<tr>
<td>Wheat straw 1</td>
<td>Peat 1, 15 %</td>
<td>-</td>
<td>342</td>
<td>7</td>
<td>I</td>
</tr>
<tr>
<td>Wheat straw 1</td>
<td>Peat 2, 15 %</td>
<td>-</td>
<td>208</td>
<td>6</td>
<td>I</td>
</tr>
<tr>
<td>Wheat straw 1</td>
<td>Peat 3, 15 %</td>
<td>-</td>
<td>187</td>
<td>5</td>
<td>I</td>
</tr>
<tr>
<td>Wheat straw 1</td>
<td>Peat 3, 15 %</td>
<td>-</td>
<td>260</td>
<td>4</td>
<td>I</td>
</tr>
<tr>
<td>Energy wood</td>
<td>medium</td>
<td>-</td>
<td>n.a.</td>
<td>75</td>
<td>V</td>
</tr>
<tr>
<td>Energy wood</td>
<td>medium</td>
<td>-</td>
<td>n.a.</td>
<td>22</td>
<td>V</td>
</tr>
</tbody>
</table>

*PB, SP, GR denotes pellet boiler, single pellet, grate reactor. AmSulf designate ammonium sulfate.*
5.2 Capture of potassium during fixed-bed combustion

Potassium release is reduced by the formation of condensed (solid and molten) ash compounds. They can be grouped according to their mineral group as: carbonates, chlorides, sulfates, silicates, aluminium silicates, or phosphates. The minerals are further composed of crystalline and amorphous phases with specific melting and decomposition points as well as vapor pressures. The aim with fuel engineering is to define a system (temperature, pressure, elemental composition) that results in a favorable phase composition. All K-containing phases that were identified throughout this work are listed in Table 10. The suitability of these phases to act as "K-capturers" varies due to their thermal stability. The mineral groups identified in this work suitable for potassium capture are carbonates, sulfates, silicates, and aluminium silicates.

Capture of potassium in silicates is commonly observed during biomass combustion of phosphorus-poor fuels, which is due to the fact that many of the "new" fuels are rich in silicon and the stability of silicates is generally high in relation to other host phases for K. There, are however eutectic temperatures at \( \sim 740^\circ \text{C} \) for the \( \text{K}_2\text{O}-\text{SiO}_2 \) system [Kracek 1937]. Ash melting and subsequent slag formation is therefore likely during K-capture by silicates. And even though smaller amounts of slag can normally be handled by the grate, care should be taken upon such attempts as discussed in paper I. Interestingly, results from paper III indicated that a large fraction of the ingoing potassium was captured by amorphous non-glass compounds rich in silicon. The stability of this (probably) meta-stable phase, however, was not determined and it is therefore not clear if such compounds should be considered as molten ash that might initiate slag formation, or if these compounds could be defined as stable end compounds within certain processes. It should also be noted that the phase composition of the silicon, \( \text{i.e.} \) if it occurs as quartz, feldspars or as amorphous silicon, might affect the reactivity of K-Si interactions [Zevenhoven 2012].

Capture of potassium in alumina silicates is an efficient way to form solid and stable compounds. The capturing efficiency has been reported to vary among different additives. Phases rich in \( \text{Al}_2\text{O}_3 \) (\( \text{e.g.} \) bauxite) have been reported to capture K, but partly due to physisorption that might lead to a re-release of alkalis [Punjak 1988, Wolf 2004]. Clay minerals richer in \( \text{SiO}_2 \) (\( \text{e.g.} \) kaolinite) have been shown to irreversibly capture the alkalis [Punjak 1988]. Clay minerals with different compositions of \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) have also been tested with the conclusion that the capturing efficiency is affected by the relative ratio among the two components [Escobar 2007]. However, such
mixtures might form molten solutions that have the possibility for a high alkali loading efficiency [Willenborg 2006], but accordingly increases the risks with slag formation. For this reason, one of the most recognized minerals for alkali capture is kaolinite. Alumina silicates are not inherent in plant biomass and need to be added by the use of certain waste streams, *e.g.* sewage sludge [Zevenhoven *et al.* 2012] and coal ash, or by additives. Even though it's more favorable to use waste streams, these sources are clearly more heterogeneous and might lack the specific alumina silicate structure that is needed for rapid reactions with potassium compounds.

Capture of potassium in *sulfates* during fixed-bed combustion was demonstrated in paper VI. The thermal stability of K-sulfates is rather high, *e.g.* $\text{K}_2\text{SO}_4$ melts at $\sim 1070^\circ\text{C}$. The biomass characterization by [Vassilev *et al.* 2010] showed that fuels with high molar S/K ratios are rare. However, sewage sludge [Zevenhoven *et al.* 2012] and peat (paper I) are sulfur-rich and could be used for this purpose. Appropriate sulfur additives, from a fuel design perspective, can be *e.g.* elementary sulfur, ammonium sulfate (paper VI), or gypsum [Piotrowska *et al.* 2015]. If the risks with increasing $\text{SO}_2$ emissions are carefully considered, sulfur could prove to be an efficient capture component for K under the right process conditions.

Capture of potassium by *carbonates* has not been studied to any greater extent, but [Olwa 2013] showed that 99 % of ingoing potassium was captured during wood gasification. $\text{K}_2\text{Ca}(_2\text{CO}_3)_2$ was identified in the ash and they proposed that it was formed by melting and dissolution of $\text{K}_2\text{CO}_3$ into CaCO$_3$ during char combustion and subsequent crystallization of $\text{K}_2\text{Ca}(_2\text{CO}_3)_2$ from a salt melt. The pure phase melts at about $\sim 820^\circ\text{C}$ [Winbo *et al.* 1998], but the stability depends on partial pressure of CO$_2$. No additives are needed for K-capture since all combustion systems contain the CO$_3^{2-}$ anion. However, the concentration of other anion forming elements need to be considered since they affect the stability of the carbonates. It is also crucial with accurate process control to avoid melt formation, decomposition, and/or high vapor pressures.

*Table 10. Summary of K-containing phases identified throughout this work in the residual ash.*

<table>
<thead>
<tr>
<th>Carbonates</th>
<th>Chlorides</th>
<th>Sulfates</th>
<th>Aluminium silicates</th>
<th>Silicates</th>
<th>Phosphates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{Ca}(_2\text{CO}_3)_2$</td>
<td>KCl</td>
<td>$\text{K}_2\text{SO}_4$</td>
<td>KAlSiO$_4$</td>
<td>Slag</td>
<td>Ca$_3\text{MgK(PO}_4)_7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{K}_2\text{Ca}_3(\text{SO}_4)_3$</td>
<td>KAlSi$_3$O$_6$</td>
<td></td>
<td>CaKPO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{K}_3\text{Na}(\text{SO}_4)_2$</td>
<td>KAlSi$_3$O$_8$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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5.3 Prediction of slag formation during fixed-bed combustion

Predictions of the slag formation have usually been performed by the use of elemental ratios, mostly applied for coals, but recently for biomass [Sommersacher *et al.* 2012]. Although such tools have proven useful, they are usually constructed based on experience and statistical considerations. In the present work another concept was applied, namely the use of the compositional triangle of $K_2O (+Na_2O) - CaO (+MgO) - SiO_2$ as shown in figure 10. This approach is based on the link between fuel compositions and melting temperatures for the major ash forming elements in biomass [Boström *et al.* 2012]. It was demonstrated in papers I and II and works well for many biomass fuels except those with high concentrations of aluminium and phosphorus. The utilization of thermodynamic equilibrium calculations for the assessment of ash melting has also been reported [Öhman *et al.* 2004a]. Such calculations require a more detailed input, but returns more detailed results, *e.g.* the phase composition and consequently the slag fraction. This will not directly imply a better prediction, but it gives better possibilities to map the sensitivity of ash melting, *i.e.* how the melt formation is affected by changing system constraints. A feature that will gain increased interest in future work is viscosity measurements. Paper II showed that apart from melt fraction, the viscosity is important as well for slag formation prediction during fixed-bed combustion. However, the use of thermodynamic equilibrium calculations in this perspective is not a straightforward approach, and requires a skilled user with continuous access to the software and updates.

The methods mentioned so far are all theoretical tools, and the only standardized experimental method is the ash fusion test (CEN/TS 15370). Here, ash samples are produced by ashing at 550°C and then formed to cylinders that are heated under oxidizing conditions. This method determines the temperatures at which the cylinders deform. However, it is criticized in the literature for poor prediction of slag results [Skrifvars *et al.* 1999]. The method was recently developed by monitoring the shape changes with a camera [Pang *et al.* 2013]. The on-line monitoring and measurements of cylinder size enabled the authors to describe the melting evolution by a sintering, an expanding, and a melting phase. However, the main issue with the method is that it does not consider fractionation of ash forming elements. This issue is overcome with lab scale bench reactors as described within the EU FP7-SME project "AshMelT". In the proposed method, a large fuel sample is combusted batch-wise in a specially designed lab-reactor and the residual ash is assessed [AshMelT 2015]. Although ash fractionation is more accurately considered, batch-wise reactors cannot reflect the slag formation severity of continuous real scale combustion units. Hence, the
ultimate test is then to conduct pilot scale experiments that also elucidate potential long term effects like accumulation of ash matter on the grate.

In the following, an attempt is made to suggest a conceptual methodology for assessment of slag formation severity on the grate during fixed-bed combustion. This description is based on the research in papers I and II, together with experiences from previous work. The four main parameters to describe by separate sub-models are: i) ash amount, ii) slag particle size distribution, iii) stickiness, and iv) grate conditions. Firstly, ash amount is described by the ash content (wt-%) by standard ashing procedure at 550°C (EN 14775). Secondly, the slag particle size distribution is probably the most difficult parameter to determine, but the melt fraction from e.g. thermodynamic equilibrium calculations is certainly one measure to use in the description. Thirdly, the stickiness could be described by the viscosity as explained in paper II. Fourthly and finally, the grate conditions should be described by simulating the fuel bed conversion through the aid of numerical modeling to supply data on both temperature and gas atmosphere profiles.
6. Conclusion

This thesis has summarized the work from the six attached papers (I-VI) relating to the issues of the formation of fine particles and slag in fixed-bed combustion of biomass. The work can be outlined as having two focus areas, (i) a more applied focus regarding fuel engineering measures for reduction of fine particle emissions and slag formation (papers I, II, IV and VI), and (ii) a more fundamental focus regarding the release of ash forming elements and the time-resolved release of potassium during biomass combustion (papers III, IV and V).

The overall conclusion related to abatement measures for particle emissions and slagging, is that the release of fine particle and deposit forming matter can be controlled simultaneously with slag formation during fixed-bed biomass combustion. This is due to the initial fractionation of K-compounds between the aerosol phase and residual ash fraction, and a further distribution of K-compounds within the residual ash in the combustor as glass, amorphous non-glass matter, and crystalline minerals. The methodology is in this perspective denoted “fuel engineering” and is based on a combined approach including both fuel design and process control measures.

The fuel engineering approach has been based on fundamental chemical thermodynamic principles in terms of melting points and vapor pressures of the compounds within the multi-phase and multi-component systems composed of the ash forming elements in the fuels at varying temperatures. One of the applied tools was the compositional triangle of the ternary system K₂O-CaO-SiO₂, which was proven particularly useful in the slagging assessments of fuels deficient in both phosphorus and aluminum. Another tool successfully applied for more detailed assessments was thermodynamic equilibrium calculations, which was used to determine the ash fractionation and thermodynamical stability of different compounds within the multi-phase ash system. A final note on the fuel engineering approach was that the fuels were normally viewed by their relative concentration of ash forming elements (K, Na, Ca, Mg, Al, Fe, Si, P, S, and Cl) on a molar basis. This enabled comparisons between basic and acidic components on a stoichiometric basis to identify possible end compounds.

The studies on time-resolved K-release showed that the Macro-TG reactor with the single pellet experiments was a valuable tool for studying ash transformation along the fuel conversion. The combination of dedicated release determinations based on accurate mass balance considerations and
ICP analysis, with phase composition characterization by XRD, is important for the understanding of K-release in general and can also give temporal data. This information will support the development of models for K-release. Presently, there seems to be a mutual agreement based on some previous work that K is released from "char-K" or from K-carbonates during wood combustion. The results presented in this work supports the release mechanism from "char-K" but questions the previously suggested release mechanism from decomposition of K-carbonates. For straw the present data support the idea of that the major part of the K-release is attributed to volatilization of KCl. The residual ash phase chemistry was, however, more complex for the straw fuel then for the wood fuel. Overall, to further explore the detailed mechanism, the novel approach developed and applied in this work should be complemented with other experimental and analytical techniques.

**Paper 1** applied fuel engineering by peat addition and it was shown to be a delicate task that required knowledge of the peat type with regards to ash content and mineral composition. Potential to reduce both fine particle emissions and slagging was illustrated in the paper. The most suitable peat type was generalized as a Carex genus with low ash content (4 wt-%) and high ratios of Al/Si and Ca/Si as well as high-reactive, fuel-inherent sulfur species.

**Paper 2** outlined the critical slag formation processes in fixed bed biomass combustion based on data from combustion experiments with 36 different woody and agricultural biomasses. Four groups with different slagging tendencies were defined based on the mass fraction of formed slag (particles >3.15 mm) during the combustion experiments. The fraction and visocisty of molten ash were found to be closely linked and be the two phenomena that explain the differences in slagging tendency for the respective fuels.

**Paper 3** showed that a single pellet reactor may act as a first tool to experimentally evaluate fuel mixtures due to the good consistency obtained between single pellet and real scale results. The effect of temperature on the presence of crystalline phases and fraction of molten ash was illustrated by two different furnace temperatures. This method supplied new empirical results on the time-resolved release behavior of ash forming elements during combustion at different temperatures. **Paper 5** complemented this study by showing the time-resolved release behavior with a higher time-resolution. Additionally, the corresponding capturing phases in the residual were determined in a similar time-resolved manner. By doing this, the single pellet method showed that
different K-capturing phases - molten ash, amorphous non-glass matter, KCl, K$_2$Ca(CO$_3$)$_2$, K$_2$Ca$_2$(SO$_4$)$_3$, K$_2$SO$_4$, KAlSiO$_4$, and KAlSi$_2$O$_6$ - were detected along the combustion sequence. The detailed phase mapping, coupled with a quantification of the release of ash forming elements, enabled a discussion about primary K-release species during single pellet combustion.

**Paper 4** investigated the use of kaolin as a mineral for capturing alkali with the residual ash, and it was shown that K was significantly captured for both the wood and the wheat straw fuels. The K capturing and release behavior upon kaolin addition, however, was different between the fuels. Kaolin was added in three levels based on chemical equilibrium calculations of the gaseous K fraction and the lowest release was achieved for the medium addition level; this was 1 and 4 wt % for wood and straw, respectively. Hence, excessive kaolin addition should be avoided due to the risk of increased coarse particle entrainment. For the straw fuel, the expected high temperature melting compounds KAlSiO$_4$ and KAlSi$_2$O$_6$ were identified and are probably responsible for the increased capture. For wood however, only trace concentrations of K/Al-silicates were identified even though the release was strongly reduced. The lack of other K containing phases points to the formation of amorphous non-molten compounds.

**Paper 6** was conducted to investigate how the release of alkali and zinc is affected by "fuel engineering", *i.e.* the combination of fuel design (additives) and process control (fuel bed temperature) during fixed bed combustion. It was shown that correct process parameter settings reduced the release, even without the use of additives. The largest reduction was achieved by the combination of fuel design and process control. It was also shown that non-optimized process control reduced the capturing efficiency of the additives. These results were of special interest for the concept of externally fired gas turbines since they showed that the release of deposit forming matter could be efficiently reduced.
7. Future work

To follow up the new findings and research questions explored within this thesis some future work can be proposed. One such activity would for example be to conduct pilot scale experiments that would focus specifically on the ash transformations occurring on the grate. One question to answer is whether long term accumulation of ash might affect slag formation on the grate during the fuel engineering situations that have been discussed in this thesis. Another follow-up study would be to more carefully characterize the aerosol properties upon fuel engineering situations. The aerosol composition, with respect to both chemical speciation and size distribution, might occasionally be strongly altered in fuel engineering situations when e.g. the release of potassium is suppressed. Thus, the aerosol characteristics should preferably initially be determined and subsequently also the deposition behavior onto heat exchanger surfaces.

Since the volatilization of ash species has been shown to be dependent on both temperature and combustion atmosphere in the fuel bed, more advanced control strategies of the fuel bed conditions are needed. This is also important to reduce and potentially avoid other ash related problems like slag formation on the grate, not at least when using more ash rich biomass fuels. In such perspective, mathematical modeling of the fuel bed would be an important support when designing and operating fixed-bed burners and boilers, for example to predict the conditions needed to predict an optimum temperature frame needed for a specific fuel engineering situation. Hence, future fuel engineering applications will probably need more advanced fixed bed burners and boilers to more efficiently coping with new problematic fuel raw materials.

The coming decades are probable to force the society into the utilization of more diverse biomass raw materials as fuels for energy purposes. Many of the fast growing energy crops as well as agricultural and industrial residues, are rich in phosphorus and this has been shown to change the ash transformations dramatically when compared to the woody and grassy biomasses used in this thesis. Predictions within these systems are difficult due to the lack of thermodynamic data, both for pure phosphates but especially for mixed systems with silicates. Hence, experimental work is needed to supply fundamental data that may be used in future applied fuel engineering situations.

The development of general models for fuel conversion of biomass would benefit from a detailed knowledge of the speciation within the fuel particle.
**Single pellet experiments with synthetic fuels** of different organic constituents (cellulose, hemicelluloses, starch etc.) and different inorganic speciation would probably enable both more accurate quantifications of the ash transformations, and isolation of certain phenomenon attributed to certain chemical reactions/speciations. This approach would enable a more direct determination of primary and secondary release speciations of ash elements.

An interesting approach to obtain fundamental data on combustion phenomenon, including the release behavior of certain ash elements, as well as to validate fuel and ash transformation models, is to **apply highly time-resolved in-situ measurements with laser-based techniques** in the thermochemical combustion and gasification research on biomass and other solid fuels. The general research focus that presently is seen, to **elucidate the combined phenomena of fuel conversion and ash transformation**, and at the same time include new fuels, comprises many scientific challenges, both of applied and fundamental character. The research presented in this thesis, has explored some of these challenges and contributed with novel methods and approaches that have gained new knowledge to be used to facilitate the development of more effective bioenergy systems.
Acknowledgements

My years as a PhD student at Umeå University (TEC-lab) are coming to an end. It’s been about five and a half years since I began my research studies and I’ve enjoyed every working day since then. Being a PhD student is really great fun! I will for sure miss these times.

To all my colleagues, it’s been a great time to work with you and many of you have also become dear friends. Cheers to you!

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References


