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# Lignocellulosic residues for bioenergy

Effects of storage, fuel design, and combustion  
characteristics

MARJAN BOZAGHIAN BÄCKMAN





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# Lignocellulosic residues for bioenergy - effect of storage, fuel design, and combustion characteristics

## Abstract

Utilization of lignocellulosic residues for bioenergy raises storage, handling, and combustion challenges. The ash-forming elements in biomass may cause ash-related problems during combustion, such as slagging, fouling, corrosion, or bed agglomeration. Most of these problems are linked to ash-chemical reactions involving alkali. The overall objective of this thesis was to evaluate the impact of storage, fuel design measures, and process adaptation for improving combustion characteristics of lignocellulosic residues to mitigate ash-related operational problems. This was done by monitoring storage-induced changes in bark influencing final material characteristics. Mechanical screening and Ca-additivation on forest and agricultural residues were done as a fuel design measure. In addition, the performance of different bed materials was evaluated in bubbling fluidized bed combustion. Significant changes in the lignocellulosic matrix near pile surfaces were observed during storage of bark, and these changes will not affect the combustion characteristics. Screening efficiently reduced the amount of ash but was associated with significant fuel mass losses and did not change the ash chemistry; thus, combustion characteristics and ash melting behavior can be expected to remain unchanged. The Ca-addition significantly increased the total defluidization temperatures but implied an elevated risk for forming corrosive species and high CO (g) concentrations. High interactions between fuel ash and quartz bed particles and low interactions between fuel ash, olivine, and feldspar bed particles were observed. The feldspar bed material reduced defluidization temperature due to the increased amount of alkali in the bed by diffusion of alkali from feldspar grains. Overall, a good understanding of the ash transformation reactions is needed to mitigate ash-related problems. In addition, fuel design measures must affect the ash chemistry in the fuel to be worthwhile.

Keywords: (lignocellulosic residues, bark storage, combustion, ash-related operational problems, ash-transformation reactions)



# Lignocellulosarester för bioenergi – effekter av lagring, bränsledesign och förbränningsegenskaper

## Sammanfattning

Användning av lignocellulosarester för bioenergi skapar utmaningar för lagring, hantering och förbränning. Under förbränning kan de askbildande elementen i biomassa orsaka askrelaterade problem, såsom slaggbildning, korrosion och bäddagglomering. Majoriteten av problemen är kopplade till ask-kemiska reaktioner som involverar alkali. Det övergripande syftet med denna avhandling var att utvärdera effekten av lagring, bränsledesignåtgärder och processanpassning för att förbättra förbränningsegenskaperna hos lignocellulosarester. Detta gjordes genom att analysera lagringsinducerade förändringar i bark och hur dessa påverkar de slutliga barkegenskaperna. Bränsledesignstudier på skogs- och jordbruksrester genomfördes med mekanisk sållning och Ca-tillsatser. Därtill utvärderades interaktioner mellan olika bäddmaterial och bränsleaska vid förbränning i en bubblande fluidbädd. Signifikanta förändringar i lignocellulosamatriken observerades i barkhögens yttre delar under lagring, dessa förändringar förväntas inte påverka förbränningsegenskaperna. Mekanisk sållning minskade mängden aska men innebar betydande massförluster och förändrade inte askkemin. Ca-tillsatsen ökade defluidiseringstemperaturerna men innebar en förhöjd risk för bildning av korrosiva komponenter och extrema CO(g)-koncentrationer. Starka interaktioner mellan bränsleaska och kvarts och svaga interaktioner mellan bränsleaska och olivin respektive fältspat observerades. Genom diffusion av alkali från fältspatkorn ökade mängden alkali i bädden, och därmed minskade defluidiseringstemperaturen i fältspatbäddmaterialet. Sammantaget behövs en god förståelse för asktransformationsreaktionerna för att mildra askrelaterade problem. Dessutom måste bränsledesignåtgärder som tillämpas påverka askkemin i bränslet för att vara lönsamma.

Keywords: (lignocellulosarester, förbränning, asktransformationsreaktioner, askrelaterade driftproblem)



*To Ellie and Filip*



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## List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I. **Marjan Bozaghian Bäckman**, Sylvia H. Larsson, Mikael Thyrel (20XX). *Evaluation of bark characteristics during storage for increased utilization in the bioenergy sector and new forest-derived materials* (Manuscript).
- II. **Marjan Bozaghian Bäckman**, Anna Strandberg, Mikael Thyrel, Dan Bergström, Sylvia h. Larsson (2020). *Does mechanical screening of contaminated forest fuels improve ash chemistry for thermal conversion?* *Energy Fuels*, 34, pp. 16294-16301.
- III. **Marjan Bozaghian Bäckman**, Anders Rebbiling, Sylvia H. Larsson, Mikael Thyrel, Shaojun Xiong, Nils Skoglund (2018). *Combustion characteristics of straw stored with CaCO<sub>3</sub> in bubbling fluidized bed using quartz and olivine as bed materials* *Applied Energy*, 212, pp 1400-1408.
- IV. **Marjan Bozaghian Bäckman**, Anders Rebbiling, Mikael Thyrel, Sylvia H. Larsson, Nils Skoglund (20XX). *Bed material performance of quartz, natural K-feldspar, and olivine in bubbling fluidized bed combustion of barley straw* (Manuscript).

Papers II-III are reproduced with the permission of the publishers.

Additional publications of relevance, although not included in the thesis:

Shaojun Xiong, Marjan Bozaghian, Torbjörn A. Lestander, Robert Samuelsson, Sven Hellqvist, Marcus Öhman (2017). Calcium oxide as an additive for both conservation and improvement of the combustion properties of energy grass: A preliminary study. *Biomass and Bioenergy*, 99, pp 1-10.

The contribution of Marjan Bozaghian Bäckman to the papers included in this thesis was as follows:

- I. Marjan Bozaghian Bäckman participated in the planning and conduction of the experiment, had a leading part in the analyses, interpretation of the results, and paper writing.
- II. Marjan Bozaghian Bäckman had a leading part in the planning and conduction of the experimental work, SEM/EDS analysis, interpretation of the results, and writing of the paper.
- III. Marjan Bozaghian Bäckman participated in the planning and execution of the combustion experiment, SEM/EDS analysis, interpretation of the results, and writing of the paper.
- IV. Marjan Bozaghian Bäckman participated in the planning and execution of the combustion experiments, performed SEM/EDS analysis, evaluated the results, and writing of the paper.

## Abbreviations

CHP	Combined heat and power plant
PM	Particulate matter
FBC	Fluidized bed combustion



# 1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) report emphasizes the urgent need to drastically reduce CO<sub>2</sub> emissions to limit the effects of climate change, which are already evident worldwide [1]. The International Energy Agency (IEA) has added a roadmap for net-zero to 2050, where bioenergy plays a major role [2]. The IPCC also highlights the importance of renewables being sustainable in terms of land use and water, and the IEA states that 100 EJ bioenergy by 2050 is within the framework of sustainable bioenergy. In 2020 the global demand for bioenergy was almost 65 EJ, of which 90% was solid biomass [2], comprising just over 9 % of the total energy demand [3].

In a Swedish perspective, the use of renewable energy sources in the energy system has increased steadily over the years, especially regarding bioenergy from lignocellulosic biomass [3, 4]. The use of biomass as an energy resource has been highly influenced by the introduction and expansion of the district heating systems in Sweden. In particular, a market has been found for forest residues that were previously not used [3, 5]. The forest industries in Sweden do not only produce forest residues; they are also together with combined heat and power plants (CHP), large consumers of this biomass residue for energy purposes.

## 1.1 Bioenergy as a source of renewable energy

Bioenergy has an advantage compared to other renewables (e.g. solar and wind power) by facilitating on-demand use as the energy is stored chemically in fuel feedstock materials and released when needed. The storage of the feedstock should preferably occur within a convenient range of thermal conversion plants. Bioenergy feedstock should be compatible with the UN's

sustainable development goals concerning energy (targets 7 Affordable and clean energy, 11 Sustainable cities and communities, 12 Responsible consumption and production) and land use (13 Climate action, 15 Life on land). This is supported by the IPCC report from 2018 on 1.5-degree global warming as a maximum value by 2050 [1]. Thermal conversion, which involves using heat with and without oxygen to convert biomass into other forms of energy, dominates the bioenergy sector, with lignocellulosic biomass being the dominating feedstock.

Lignocellulosic biomass refers to a wide range of plant-based materials - composed of cellulose, hemicellulose, and lignin in various proportions - that can be used as feedstock for bioenergy. The chemical composition of lignocellulosic biomass (carbon, hydrogen, and oxygen) enables it to be used directly for, e.g. renewable heat and electricity or processed further, e.g., bioethanol or biogas production. Utilizing bioenergy from lignocellulosic biomass - especially from residues from forestry, agriculture, and related industries - is an important strategy for reducing CO<sub>2</sub> emissions and increasing sustainability in the energy sector [2]. Residues do not compete for land area with food production and can be locally available, enhancing energy security and local job opportunities.

Utilization of a larger share of the wood and crop already harvested may be a key factor in the global energy transition towards more renewables. In Sweden, refined wood fuels (e.g., sawdust, wood chips, wood pellets, briquettes, and wood powder) are predominantly used [5-7]. Increased utilization of unrefined wood fuels (e.g., branches, tops, and bark) along with agricultural residues would enable an expansion of the total available biomass fuel feedstock.

However, not all biomass residues can – or should – be used in bioenergy processes as they could impact soil nutrient recycling or quality [8-11]. Residue feedstock assortments may introduce more potentially problematic materials from an operational point of view for the energy conversion system. Compared to traditionally used stem wood, these assortments vary widely in composition, both in chemical and physical properties [12-16]. Below, the different types of biomass fuels covered in this thesis, challenges associated with the respective fuels, and suggested measures are presented.

## 1.2 Lignocellulosic biomass residues

### 1.2.1 Forestry residues

Solid biofuels, predominantly from the forestry sector, comprised most of the bioenergy supply globally in 2018 [17]. The same report details that in most industrialized countries, solid biofuels for energy production from the forestry sector (forest harvesting and wood processing industries) are sourced from residues.

In Sweden, the forestry sector generates large quantities of residual streams such as logging residues, bark, wood chips, wood shavings, or sawdust [18]. In 2020, forest residues from the forestry sector used as wood fuels for energy supply, mostly in Swedish district heating systems and combined heat and power plants (CHP), accounted for 54,5 TWh [3]. This corresponds to 39% of the biofuels used in the Swedish energy system that year and 11 % of the total energy consumed [3].

The majority of the produced forest residues in Sweden originate from the wood processing industry, where high-value products like lumber, pulp, or paper are produced [19]. The wood processing industries are not only producers of forest residues as a residual stream but also large consumers of these residues. The internal use of produced forest residues in the wood processing industries constitutes a large part of the total Swedish bioenergy - making them the largest consumer of wood fuels, followed by the Swedish district heating systems as well as combined heat and power (CHP) plants [3].

Currently, in Sweden, several different types of forest residues are used as wood fuels in energy production. They can be classified into *uncomminuted* wood fuels originating from forest harvesting (logging residues as branches, tops, and stumps) or *comminuted* wood fuels from the wood processing industry (bark, sawdust, wood chips, and wood powder). Sawdust and wood chips were the primary wood fuels used in the district heating sector in 2019 [6]. Since the wood processing industry uses biomass consisting of residues and by-products produced at the industries internally, district heating systems that consume large volumes of biomass have to import biomass to some extent, mainly wood chips and wood pellets, to maintain a sufficient supply [5].

A major difference between comminuted and un-comminuted wood fuels is that the latter is more structurally heterogenic (high bark content, contains needles, inclusions from sand and soil) and has a lower bulk density and energy content. These fuel characteristics introduce challenges in utilizing these un-comminuted wood fuels from forest harvesting in energy conversion, which is discussed further in section 1.3.3.

### 1.2.2 Agricultural residues

Agricultural residues have the potential to contribute to the annual bioenergy supply without increased competition in land utilization [20]. The utilization of agricultural residues for energy conversion at a global level is poorly known, as few countries collect data on the actual production and use [21]. Due to the large cultivation of straw-producing crops in Denmark and specific governmental incentives, straw has become an important residual biomass resource in the Danish energy system [22, 23]. Further, it is estimated that 140 million tons are annually combusted on fields in China [24], making it clear that the strategies for utilization of biomass can be both improved and increased.

In Sweden, the main agricultural residues used for heat production are straw from cereals (barley and wheat) and oilseed production (rapeseed), as investigated by Bentsen *et al.* [22]. The study further found that these residues are usually fired in small-scale boilers, although a few large-scale boilers, including CHP plants, burn straw [22]. The contribution to heat production from such feedstock is low on a national level [22]. Straw as a fuel in Sweden is often used by farmers who themselves are producers of these residues [22, 25]. The lack of available statistics for heat production from straw, including straw prices, collection, and amount of straw used, arises from the lack of an established market in Sweden [22]. The market for agricultural residues for bioenergy is not as established as in the case with forest residues in Sweden due to the high availability of wood fuels and contributing factors, including established harvest practices, logistic systems, and better combustion properties of wood fuels. Also, in Sweden, straw for bedding and feed is often prioritized before other uses.

However, a study on the potential increase in biomass supply in Sweden by 2050 estimates an increase in agricultural residues for bioenergy production, primarily the potential for straw as fuel for heat or power

production compared with current use [25]. Somewhat dated reports on the potential availability of straw for bioenergy purposes suggest that up to 20 TWh could be grown on arable areas unused in 2008 and that up to 4 TWh of agricultural residues was available for bioenergy purposes in 2009 [26, 27].

## 1.3 Challenges when utilizing forest and agricultural residues as solid biofuels

### 1.3.1 Biomass feedstock from a market perspective

There are market challenges in using forest and agricultural residues for bioenergy purposes. Although they are considered low-cost biomass, there are additional costs associated with harvesting, transporting, storing, and the subsequent energy conversion processes [28-32]. These residues typically have low energy content, high moisture content, high ash content and may contain sand and soil inclusions, which adversely affect combustion properties [12, 13, 31, 33, 34]. Due to these properties, the lignocellulosic residues are often considered low-quality solid biofuels where the main challenge is the heterogeneity from a market perspective.

Forest and agricultural residues may therefore benefit from additional pre-treatment aiming to convert low-quality fuels into higher-value fuels with properties requested in the fuel market. Such properties include characteristics such as an improved energy density, lower and more consistent moisture content, and a manageable ash content. This can be achieved by pelletizing, briquetting, screening or other pre-treatment strategies [35-40]. This may involve a complex chain of advanced processes and ultimately not be cost-effective despite improving the indicators mentioned individually.

### 1.3.2 Storage of solid biofuels

For energy conversion, a difference in the supply and demand of solid biofuels often occurs since the need for heat and energy is highest during the winter. To ensure a constant supply of solid biofuels due to seasonal availability and facilitate handling, the biomass is usually stored until utilization [41]. Also, the lower heating value and bulk density of solid

biofuels, compared to e.g. coal, implies that large volumes need to be stored for a given amount of energy. The storage should ensure a maintained quality of the solid biofuel, limit dry matter losses, and reduce the risk of fires due to self-ignition. Biomass storage is, therefore, a critical step in the biomass supply chain as an efficient storage method must preserve both the quantity and quality of biomass.

Several different storage methods exist, ranging from un-comminuted material stored in the field or forest to comminuted material stored at industrial sites. During storage, the properties of the solid biofuels changes due to biological, chemical, and physical processes, which may adversely affect fuel quality and implicate certain risks such as self-ignition [42-44]. Dry matter loss, risk of self-ignition, and health risks caused by high concentrations of allergenic microspores in the air are well-known issues regarding biomass storage [32, 44, 45].

Moisture content, temperature, pH value, particle size, and microbial activity affect a solid biofuel during storage [46, 47]. As a result, loss of dry matter, calorific value, and ash content can be considered parameters affected by the storage conditions. If the conditions are suitable during biomass storage, e.g., nutrients, moisture content (> 20%), temperature (15-45 °C), and available oxygen, colonization and decay by various microorganisms can occur, resulting in dry matter losses [32, 43, 48-51].

The rate at which degradation by microorganisms occurs and the types of microorganisms (fungi and bacteria) that exist depend on the type of biomass, temperature, moisture, amount of nutrients, oxygen, particle size, pile dimensions and storage duration [43-45]. Despite the great diversity of microorganisms that degrade biomass, fungi are superior to bacteria in decaying the lignocellulosic matrix [43, 50-52]. When fungi consume organic matter, they also produce fungal spores that may pose environmental and hygienic problems as well as heat, leading to increased risks of self-ignition. In fresh biomass, respiration by the living parenchymal cells can contribute to the initial heat development [43, 51]. Therefore, biological activity is an important factor in storage regarding dry matter losses, self-ignition, and work environment during handling starting already with the freshly harvested biomass.

### 1.3.3 Pre-treatment of lignocellulosic residues for bioenergy

Pre-treatment in the context of this section refers to fuel preparation for thermal conversion of forestry and agricultural residues. Objectives of pre-treatment for fuel upgrading are often to facilitate transportation, storage, and the subsequent energy conversion process. They may involve densifying the biomass, resizing particles to match the demands of a process, and/or reducing the amount of sand and soil inclusions.

The preferred fuel quality for thermal conversion of solid biofuels often depends on the size of the heating plant, where large-scale plants (>50 MWth) are less sensitive to fuel quality than small-scale district heating plants (<1 MWth) [53, 54]. Smaller facilities often impose more restrictive fuel quality specifications as they are more sensitive to fuel parameters such as moisture content, ash content, heating value, particle size, and amount of sand and soil mineral inclusion [55-58]. Consequently, appropriate pre-treatment for fuel quality upgrading of solid biofuels may sometimes be required to meet the requirements of, mainly, small-scale plants and residential boilers.

The inhomogeneous particle size and shape of biomass particles significantly influence the handling operations and feeding systems as well as the subsequent thermal conversion for solid biofuels, especially forest residues [59-61]. The size and shape of solid biofuel particles affect the flowing properties in feeding systems, causing blockage and bridging [62]. The particle size is also of importance during storage conditions of solid biofuels as it influences the drying time and may contribute to a high surface area for microbial activities [32]. Uniform size and shape are important to fuel quality parameters that often need to be addressed for bulky biofuels such as forest residues.

Forest and agricultural residues are commonly associated with sand and soil inclusions as a result of harvesting practices, where soil and sand minerals can be carried and mixed with the raw material during extraction and roadside (forest) or field (agriculture) storage [63, 64]. Such inclusions increase the overall ash content and may negatively impact the combustion behaviour depending on thermal conversion technology [31]. Therefore, it is often necessary to elucidate the chemical and physical properties of potential fuel feedstock for thermal energy conversion by fuel analysis, including not

only heating values or moisture and ash content, but also the inorganic elements present in the ash.

### 1.3.4 Thermal energy conversion of lignocellulosic residues

#### 1.3.4.1 Thermal conversion of the lignocellulosic matrix

During thermal conversion of lignocellulosic biomass, the organic structure of the biomass is decomposed while the inorganic fraction undergoes several complex chemical and physical transformations. The ash-forming elements are either released to the gas phase as condensable vapor species (forming fly ash or deposits), entrained as solid particles (coarse fly ash), or remain as non-volatile solid residue (bottom ash) [65]. The outcome of the inorganic fraction depends on the composition and concentration of the individual ash-forming elements, the overall ash content, process conditions, and which thermal energy conversion technology is employed.

The main thermal conversion processes are pyrolysis (production of combustible gases, pyrolysis oil, and biochar), gasification (production of combustible gases and heat and power generation), and combustion (heat and power generation) [66]. The temperature and oxygen conditions can be controlled to achieve different thermal conversion processes; the solid biofuel may undergo pyrolysis, gasification, or complete combustion, where pyrolysis is an important first step in gasification and combustion.

In combustion, a solid biofuel particle is introduced into a heated environment and undergoes different overlapping conversion stages: drying, devolatilization, and char combustion (Figure 1). During the drying phase, the existing water in the biofuel starts to evaporate. After drying, as the temperature increases, devolatilization (pyrolysis) converts the solid biofuel into gases (a fraction of ash-forming elements is volatilized and released to the gas phase) and a carbon-rich char. As the temperature increases in the final char combustion phase, the char is oxidized at relatively high temperatures until combustion is completed, leaving the non-volatile ash-forming elements, i.e., ash, as a residue.

If the oxidizing agent available is insufficient for complete combustion, gasification follows where both heat and combustible gases are produced with small amounts of remaining char. In contrast, combustion will follow with heat and flue gas as the principal product if the oxidizing agent is

sufficient, i.e. greater than the stoichiometric supply for complete combustion. The ash-forming elements will be distributed in the formed ash fractions – i.e., bottom or bed ash, coarse fly ash, and particulate matter. Their chemical speciation and fractionation are affected by reactions of the ash-forming elements.

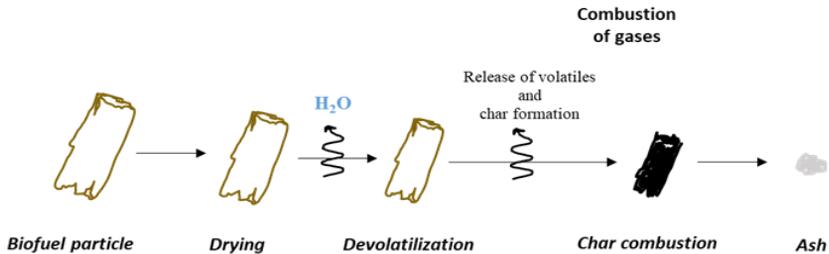


Figure 1. Simplified combustion stages of a solid biofuel particle.

#### 1.3.4.2 Ash transformation reactions

There is great variability in ash-forming elements between different solid biofuels (e.g., stem wood, logging residues, bark, straws) and within a certain solid biofuel [13, 16]. This inconsistency arises from varied growth conditions and handling. As the ash-forming elements may contribute to different ash-related problems, it is therefore crucial to know how they interact. The main ash-forming elements important for thermal conversion processes can be limited to Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, and Mn, where Si, Ca, and K are often most dominating [67]. During thermal conversions of solid biofuels, complex ash transformation reactions involving the ash-forming elements occur [67, 68].

Boström et al. [67] describe the ash transformation reactions by dividing the reactions into primary and secondary reactions. In this thesis, due to the high complexity of these reactions, this will be described in simplified terms to facilitate the structuration of ash-forming elements and their formed products. The primary reactions are assumed to occur during the devolatilization phase and involve the oxidization of ash-forming elements resulting in simple oxides – primary oxides. More correctly, as described by Boström et al. [67], primary reactions are based on the equal affinity of oxygen towards both the carbon-hydrogen matrix and the ash-forming elements, i.e., arranged according to their reactivity (Figure 2).

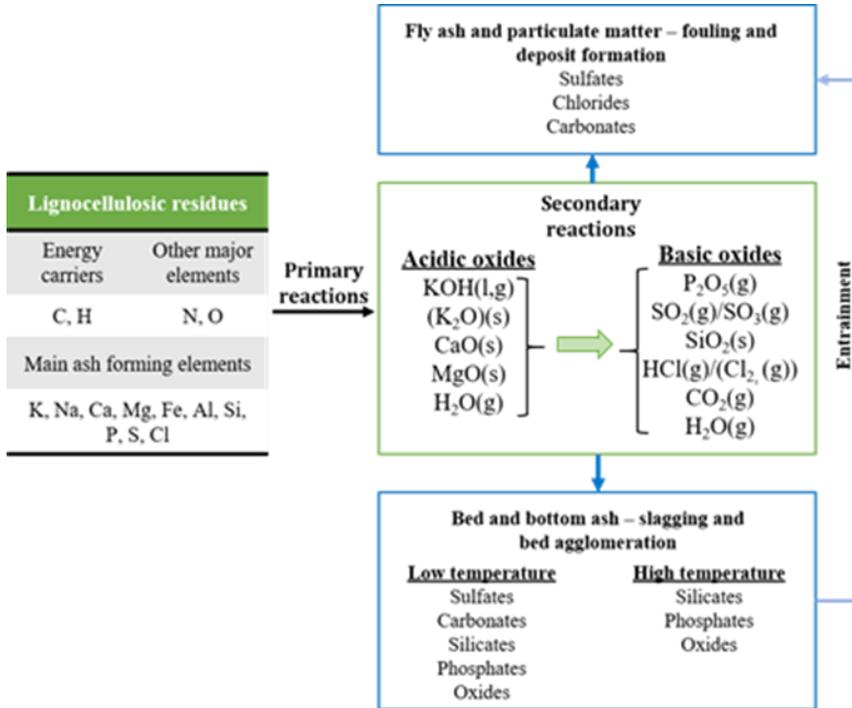


Figure 2. Simplified schematic description of the ash transformation reactions according to the division into primary and secondary reactions as defined by Boström et al. [67], including ash fractions where the resulting reaction products are commonly observed.

The secondary reactions intend to describe the transformation of the formed products by the primary reactions, i.e. the transformation of the primary oxides where a single element type is bonded to oxygen where K<sub>2</sub>O, CaO, or SiO<sub>2</sub> are examples of particular importance in ash from lignocellulosic residues. To simplify the scheme of secondary reactions, the formed primary oxides can be divided into two categories – acidic oxides and basic oxides (Figure 2). These acidic and basic oxides are assumed to react further in secondary reactions to form joint compounds other than oxides. The generalized thermodynamic reactivity of each of these components is represented by their position in the respective columns (see Figure 2), where components higher up are considered more reactive [67].

Consequently, KOH will primarily form phosphates until P<sub>2</sub>O<sub>5</sub> is depleted, then sulfates will form until SO<sub>2</sub>/SO<sub>3</sub> is depleted, followed by silicates, chlorides, and carbonates, and when all KOH is consumed,

according to Figure 2, NaOH will react in the same manner and so on. Similarly, if there is an excess of  $P_2O_5$  in comparison to KOH, it will react with NaOH, and so on. As stated, this is a simplification of the reactions taking place during thermal conversion of biofuels; however, it serves the purpose of facilitating the understanding of the initial ash transformation reactions. The reaction products from secondary reactions may, of course, react further to form more complex compounds.

#### 1.3.4.3 Ash-related problems regarding combustion of solid biofuels

Ash transformation reactions may cause different ash-related operational problems during thermal conversions such as slagging, fouling, corrosion, formation of tars (pyrolysis and gasification), or bed agglomeration in fluidized bed boilers. [34, 69-76].

Slagging mainly occurs in the primary conversion chamber of a boiler (i.e., the high-temperature zones of the boiler) and is related to the melting properties of the ash. Slag formation is affected by both the chemical composition of the ash and the combustion temperature [34]. However, if the ash in the chamber begins to melt, whereupon slag is formed, the slag can cause problems by hindering the supply of air and fuel as well as ash removal during thermal conversion. The formation of slag mainly depends on the concentrations of K, Ca, Si, O, and to some extent, Al, as they are found to be the main constituents of slag from the combustion of fuels with similar compositions as forest and agricultural residues, suggesting that slag mainly consists of different silicates [34, 67, 73, 74, 77]. Slag formation is suggested to be initiated by gaseous K-species reacting with Si (inherent or via inclusion) during the devolatilization and char burnout phase, forming low-melting sticky K-rich silicate melts [74]. Consequently, sand and soil inclusions will therefore further increase the slag formation risk [31]. In contrast, Ca and Mg (if present) can react with the formed sticky K-silicate melts to form high-temperature melting Ca-silicates; as a result, K is released into the gas phase [78, 79].

Fouling, on the other hand, refers to deposits formed in the lower-temperature zones of the boiler and involves condensation (while the gases cool down) and deposition of solid ash particles, i.e., particulate matter (PM) [76]. The formation of condensable salts is suggested to be due to volatilized

K that undergoes different gas-phase reactions forming these salts that may condense out on boiler surfaces causing deposits and corrosion [76].

Bed agglomeration only occurs in fluidized-bed boilers as it involves the formation of agglomerates of bed material and ash due to sticky layers existing, namely coatings, on the bed materials and/or molten ash particles [80]. Similar to slag formation, which often depends on the chemical composition of the ash and the combustion temperature, bed agglomeration also depends on the type of bed material employed [81]. Generally, bed agglomeration mechanisms could be classified as “melt-induced” or “coating-induced” [70, 80, 82]. In the “melt-induced” mechanism, the bed material particles are “glued” together with fuel molten ash particles, while in the “coating-induced” mechanism, a coating is formed on the bed material particles, and the agglomeration is initiated by “neck-formation” between the coated bed material particles. Both mechanisms, however, initiate the process of agglomeration by interactions between bed material particles with the fuel ash, resulting in bed defluidization, which may cause severe and costly problems.

The alkali metals in biomass, mainly K, play an important role in ash-related problems since much of the K in the fuel is volatilized under the high temperatures of combustion, which can result in undesirable reactions [79]. The K may react with Si (inherent or via inclusions), resulting in the formation of low-melting sticky K-silicates (formation of slag), or with S or Cl forming condensable salts, i.e.  $K_2SO_4$  and KCl that can be found as particulate matter (PM) or deposits on boiler surfaces (fouling). Consequently, most of the ash-related problems during combustion of solid biofuels are associated with reactions involving alkali metals [14, 74, 77, 83, 84].

## 1.4 Measures to increase and streamline the use of forestry and agricultural residues as solid biofuels

### 1.4.1 Storage of solid biofuels

The location of the storage site and the storage option commonly depend on the solid biofuel assortment (e.g., biomass type and whether the biomass is comminuted or un-comminuted) and the availability of storage space. Field

storage often involves the storage of un-comminuted biofuels such as branches and tops directly after felling or harvest [63, 64, 85]. Storage at plant sites or terminals often involves the storage of comminuted biofuels (e.g., bark, chips, and powder) [41, 64]. Low-cost storage methods are typically chosen for biomass intended for bioenergy applications and may involve non-covered or covered storage [86-88]. These studies have shown that covering can protect biomass from rewetting by precipitation during storage thereby resulting in lower biomass losses [47, 86]. To reduce dry matter losses and the risk of self-ignition, the material should be comminuted close in time to utilization as larger particles allow better ventilation inside the pile, which can reduce microbial activity with less specific area for microorganisms to attack and the risk of self-ignition [32, 64, 89].

For agricultural residues to be used for thermal conversion, field drying is often first employed to mitigate the negative effects of high moisture content. After drying, agricultural residues used as biofuels generally are most commonly densified into either square or round bales, which is considered the most cost-effective method [90, 91].

#### 1.4.2 Pre-treatment of solid biofuels

A mechanical screening operation can be performed to overcome some of the physical property limitations regarding the size, shape and the amount of sand and soil inclusions of, especially for woody fuels. The objectives of mechanical screening operations are to upgrade the solid biofuel quality by producing a fuel with more suitable properties for effective combustion. Resizing solid biofuels to a uniform size improves the flowability and the handling properties as it reduces the amount of oversized particles, which may cause problems with regard to conveyors and feeding systems of heating plants [59, 92], whereas reduction of fine particles and removal of contaminations improves the combustion properties [31, 61, 73]. Besides, the particle size also influences storage properties such as drying rate and the emergence of microorganisms and thereby the durability of the stored biofuel [50, 51, 89].

Although screening, in many studies, has been demonstrated to be effective and profitable for fuel upgrading to a commercial standard [37, 38, 56, 93], screening biofuels for thermal conversion is not a generalized practice. Nevertheless, several screening strategies can be used for biofuel

upgrading, including star screening, deck screening, drum screening or disc screening.

### 1.4.3 Combustion of solid biofuels – fuel design

Ash-related problems can be mitigated by altering the chemical composition of the fuel intended for combustion in the present work, by different strategies. These include pre-treatment of biomass by strategies such as washing to reduce alkali content [94], additivation of materials with no heating value [95-99], but also include co-conversion of different lignocellulosic biomasses and residual streams [100]. As alkali metals, in particular K, play an important role in ash-related problems, the focus of mitigation measures is often dedicated to alkali. To mitigate ash-related problems specifically caused by alkali species in biofuels; the alkali can be removed as alkali chlorides by leaching [101, 102], use of alkali binding additive or mixed with other fuels for better ash composition [96, 97, 103-107], or in case of fluidized bed combustion, use bed materials that interact less with biofuel ash [108, 109]. These strategies primarily aim to reach an ash composition permitting predictable operation of the thermal conversion process, although they might be further developed to include desirable ash qualities for purposes such as phosphorus recycling.

The purpose of additive use is to alter the chemical composition of the biofuel to create ash compositions that are predicted to mitigate ash-related problems during combustion. Several studies have been performed on the use of additives to improve combustion characteristics, that is, decreased slagging tendency, deposit formation and corrosion by reacting with biofuel alkali, converting it to less deleterious compounds [96, 97, 104, 106, 110].

Additives typically used in bioenergy applications could be sorted in three main categories: calcium, sulphur, or aluminosilicates. According to some studies, the most used and well-described additives for reducing slagging tendencies are those containing lime (i.e., Ca-based) or clay minerals (i.e., aluminosilicates-based) [96, 111]. Both Ca-based and aluminosilicate mineral additives commonly promote the formation of alkali-containing compounds with higher melting temperatures than observed in the unmodified fuel ash, thereby forming either potassium-calcium silicates or potassium-aluminium silicates in the bottom ash or bed (in the case of FBC) which have higher melting temperatures than pure potassium-silicates.

Consequently, particulate emissions may be reduced by the alkali capture, especially in the case of clay mineral additives. The sulphur additive category mainly affects the fouling and deposit formation by promoting alkali sulphate formation rather than alkali chloride formation, reducing the risk of severe high-temperature corrosion [112].

The  $\text{Ca}^{2+}$  present in Ca-based additives may substitute alkali in potassium silicate melts which results in alkali species being volatilized and becoming available for subsequent gas-phase reactions [78, 113]. Thus, making Ca-based additives more efficient in reducing bottom ash slagging and sintering than reducing deposits and corrosive species in the flue gas. The effect of Ca-additives has been studied in several studies to improve ash-melting temperature and reduce the risk of slag formation [96, 104, 114]. The choice of additive is based on the overall composition of the biofuel ash. Nevertheless, the choice is not always straightforward. The main challenge is choosing an additive that mitigates ash-related problems in a real combustion environment that involves not only complex ash transformation reactions of the solid biofuel ash, but also the transformation/stability of the additive, which is both affected by combustion temperature and residence time [67, 73, 75, 113]. The cost and availability of an additive should also be considered. However, the use of additives in this case to mitigate ash-related problems is a balancing act between retaining alkali in bottom ash and releasing it into the flue gas as emitted PM or volatile species.

#### 1.4.4 Interactions of fuel ash and bed material

In fluidized bed combustion, the use of bed material that interacts less with biofuel ash is another approach to mitigate ash-related problems. The most used bed material is quartz (also known as silica-sand) [70]. Using quartz bed particles when burning biofuels may result in layer formation consisting mainly of K- and Ca-silicates that may form a molten viscous phase on the bed particles, thus making the particles sticky [70, 71, 80, 115]. Therefore, changing bed material from silica-containing quartz into alternative ones without silica is an alternative approach that may reduce interactions between bed material particles and the K and Ca in the solid biofuel during combustion. Alternative bed materials have been suggested and studied, showing a lower agglomeration tendency in fluidized bed combustion and gasification [108, 109, 116-120]. However, compared to quartz most of the alternative bed materials may be more expensive thus making quartz the

dominating bed material used even with high alkali biofuels. Low-cost bed materials are of interest as the bed material needs to be continuously replaced with fresh bed material during combustion to retain efficient combustion conditions. As a result, bed material cost and availability are important factors when choosing a bed material.

## 1.5 Objectives

The overall objective of the research presented in this thesis is to evaluate the impact of storage or pre-treatment as fuel design measures, and process adaptation for improving the combustion characteristics of lignocellulosic residues with emphasis on fuel ash chemistry and demonstrate its relevance in industrial bioenergy applications. The research aims to improve fuel flexibility and mitigate ash-related operational problems in existing and future combustion appliances.

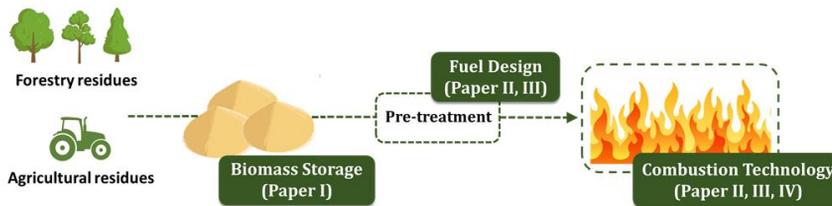


Figure 3. Schematic overview of the work flow of the thesis.

This was achieved through storage and combustion studies. This thesis can therefore be divided into the following specific sub-objectives:

- To monitor large-scale storage-induced changes in bark to clarify patterns and interactions influencing final material characteristics
- To investigate the impact of fuel design by screening with a focus on ash transformation reactions
- Investigate the impact of fuel design by  $\text{CaCO}_3$  additivation during storage on combustion characteristics of barley straw
- Evaluate the performance of different bed materials in bubbling fluidized bed combustion of agricultural residues

## 1.6 Overview of appended papers

This thesis is based on four papers that contribute to the general body of knowledge on storage, pre-treatment as a fuel design measure, and process adaptation in the combustion of lignocellulosic residues. Table 1 presents the outline of the thesis.

Table 1. Outline of studies upon which this thesis is based.

<b>Paper</b>	<b>Biomass</b>	<b>Target</b>	<b>Approach</b>	<b>Application</b>
I	Spruce bark	Evaluate bark property changes	Storage monitoring	Large-scale storage
II	Forest residues	Improved combustion properties	Pre-treatment/ Fuel design	M-TGA combustion
III	Barley straw	Improved combustion properties	Pre-treatment/ Fuel design	Fluidized bed combustion
IV	Barley straw	Agglomeration mechanism and bed interaction	Process adaptation	Fluidized bed combustion

### 1.6.1.1 Paper I

This study aimed to evaluate changes in bark material properties in different locations in a pile during storage. Despite high temperatures and moisture contents, only minor changes in bark material properties were observed. The most significant differences were observed near the pile surfaces, where changes in the lignocellulosic matrix were observed. However, these changes will not affect the combustion characteristics of the stored bark but may affect other processes.

### 1.6.1.2 Paper II

The effect of mechanical screening pre-treatment as a fuel design measure for fuel quality improvement of forest residues, with emphasis on ash chemistry, was evaluated. Screening efficiently reduced the amount of ash and fines but was associated with significant fuel mass losses. However, screening did not change the ash chemistry; thus, the combustion characteristics and ash melting behavior can be expected to remain unchanged.

#### 1.6.1.3 Paper III

The combustion characteristics of barley straw pre-treated and stored with  $\text{CaCO}_3$  as a fuel design measure, based on a combined improvement of the storage and combustion approach suggested by Xiong et al. [40], were empirically evaluated in bubbling fluidized bed combustion using quartz and olivine as bed materials. The Ca-addition significantly increased the total defluidization temperatures for both bed materials, but an elevated risk for the formation of corrosive compounds and high CO (g) concentrations were observed. Therefore Ca addition to alkali-rich biomass must carefully consider the overall impact on the combustion process as a reduction of slagging or agglomeration may not improve other relevant parameters.

#### 1.6.1.4 Paper IV

The study evaluated the performance of quartz, olivine, and feldspar as bed materials in bubbling fluidized bed combustion of barley straw used as a model agricultural residue. The bed materials were evaluated based on interactions with the fuel ash by studying layer formation and the formed agglomerates. High interactions between fuel ash and quartz bed particles and low interactions between fuel ash and olivine and feldspar bed particles were observed. The feldspar bed material caused an early bed agglomeration at a low defluidization temperature due to extensive adhesive layer formation on included quartz bed grains, potentially caused by the diffusion of alkali out of feldspar grains coupled with Ca migration and the quartz particles present in the bed material. Overall, this would suggest that olivine could be the better choice of the bed materials tested in prolonged operation and that feldspars may not be suitable as a quartz replacement in thermal conversion of straw-type fuels, which requires further investigation.



## 2. Material and methods

### 2.1 Overview of materials and methods

The thesis contains four studies on storage and combustion-related problems when using lignocellulosic residues from forestry and agriculture as solid biofuels. The chosen model feedstocks (Norway spruce bark, forest residues, and barley straw) represent relevant fuels for a variety of regions. The specific fuels, experimental setups, lab equipment, and characterization methods utilized in the individual studies (I-IV) are summarized in Table 2.

Table 2. Overview of fuels and analytical methods used in the work presented in papers I-IV.

		I	II	III	IV
<b>Materials</b>					
Norway spruce ( <i>Picea abies</i> ) bark		X			
Forest residues - mix of Norway spruce ( <i>Picea abies</i> ), Scots pine ( <i>Pinus sylvestris</i> ), and birch ( <i>Betula ssp.</i> )			X		
Barley straw ( <i>Hordeum vulgare</i> )				X	X
<b>Experimental approach</b>					
Large-scale storage		X			
Fuel design - Screening			X		
Fuel design - Additive				X	
Process adaptation – Bed materials					X
<b>Combustion techniques</b>					
Macro-TGA			X		
Bubbling Fluidized Bed (BFB)				X	X
<b>Chemical Analysis</b>		<b>Standard/method</b>			
Moisture content	ISO 18134	X	X	X	X
Ash content	SS-EN ISO 18122:2015a	X	X	X	X
pH	Sithole [121]	X			
Wood polymer composition analysis	Method described by Hayes [122]	X			

DNA sequencing	Novogene	X		
Calorific value	SS-EN ISO 18125:2017		X	
PSD	ISO 17827-1:2016		X	
Main ash-forming elements (K, Na, Ca, Mg, Fe, Al, Si, P)	SS-EN 13656		X	
Main ash-forming elements (K, Na, Ca, Mg, Fe, Al, Si, P)	SS-EN 15290:2011		X	X
C, H, N	SS-EN ISO 16948:2015		X	X
Chlorine (Cl) and Sulphur (S)	SS-EN 16994:2015		X	X
Oxygen (O)	SS-EN 14918:2010		X	X
<b>Characterization methods</b>				
SEM-EDS			X	X X
Powder XRD			X	X

<sup>a</sup>Reported as SS-EN 14775:2009 in papers III, and IV, standard later replaced by SS-EN ISO 18122:2015.

The solid biofuels presented in the papers included in this thesis (Table 2) span a variety of different residues where bark and forest residues were used as model raw materials from the forestry sector. In contrast, barley straw was used as model raw material from the agricultural sector. Additionally, all fuels originate from typically Scandinavian species of both wood-based and agricultural origin. The fuels were chosen to cover the spectra of fuels utilized on the fuel market today. Details regarding the specific biofuels can be found in the respective papers.

Furthermore, all fuels in papers II-IV were pelletized (8 mm) using conventional pelletizing equipment before combustion. An in-house single pellet press and procedure, designed and developed by Nielsen et al. [123], was utilized to mimic commercially produced pellets combusted in papers II, III and IV.

## 2.2 Experimental setups and sampling

### 2.2.1 Storage-induced changes in bark

In paper I, approximately 450 m<sup>3</sup> of fresh Norwegian spruce (*Picea abies*) bark originating from a sawmill was used to construct a large-scale pile with approximate dimensions of 17.6 × 12.5 × 3.5 m (length × width ×

height). The bark pile was divided into three sections to allow cross-section sampling after 4, 12, and 24 weeks (Figure 4). Each cross-section had four sampling points denoted S (on the side), C (in the center), T (at the top), and B (at the bottom). To monitor the temperature development during storage, four thermocouples were mounted in the sampling points S, C, T, and B at the cross-section for week 24.

On the day of pile construction, several sub-samples of the fresh bark were pooled. The pooled samples were reduced into a single representative sample by systematic sample division. During storage, the material sampling was performed in sampling points denoted S, C, and T (Figure 4) at the cross-sections on weeks 4, 12, and 24. At each sampling week, three replicates of 10 liters and one sample of 500 g were taken from the sampling points S, C, and T. The smaller sample was immediately frozen for wood polymer composition and DNA-sequencing. Subsequently, the entire section corresponding to a specific sampling week was removed from the pile and discarded. The pile dimensions, sampling points, and thermocouple locations are shown in Figure 4.

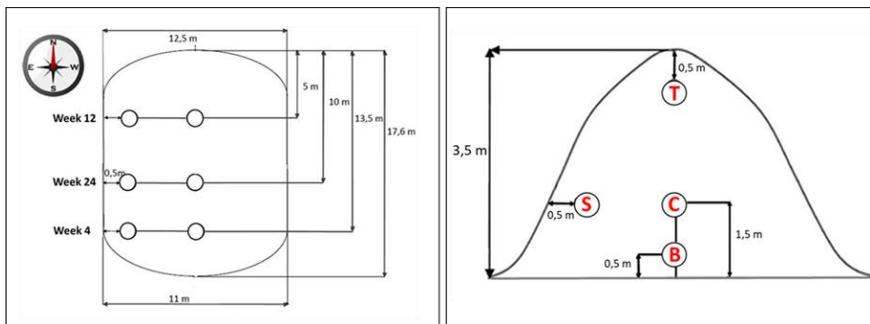


Figure 4. Dimensions, sampling points, and thermocouple locations of the constructed spruce bark pile a) seen from above, and b) cross-section of the bark pile showing the location of sampling points in weeks 4, 12, and 24.

### 2.2.2 Fuel design measures

In papers II and III, different pre-treatment approaches (removal or addition of ash forming elements) were tested as fuel design measures to create ash compositions predicted to mitigate ash-related operational problems during the combustion of lignocellulosic residues as solid biofuels.

In Paper II, a mobile star screen (Backer 3-mal, Backers Maschinenbau GmbH, Twist, Germany) was used to design a fuel with more appropriate ash content and ash characteristics for combustion by screening a forest residues with high levels of sand and soil inclusions. Approximately 2.4 metric tons (t) of forest residue chips were screened at each of the six configurations tested concerning different rotational speeds and a supplementary windshifter (Norditek VS1200, Norditek, Sävar, Sweden) for the removal of stones and sand minerals. Each machine setting used resulted in three size fractions; fine (< 3 mm), medium, denoted *accept* (3 – 45 mm), and coarse (> 45 mm). Only the accept fractions were used for combustion experiments, and the fine and coarse fractions were rejected. The screening resulted in six accepts fractions from each machine setting (Table 3) denoted M80, M90, M100, MW80, MW90, and MW100, where the number was derived from selected rotational speed relative to maximum (100%) and W annotates the presence of a windshifter. Fuel and combustion properties were determined for the six accepted fuel fractions, and the non-screened material denoted NS. The schematic overview of the workflow in paper II is shown in Figure 5.

Table 3. Screen settings tested (M=only star screen, MW=star screen+windshifter).

<b>Screen setting</b>	<b>Rotation speed of the stars (% of maximum speed)</b>	<b>Speed of the feeder (% of maximum speed)</b>	<b>Windshifter</b>
NS	N/A	N/A	No
M100	100	80	No
MW100	100	61	Yes
M90	90	80	No
MW90	90	61	Yes
M80	80	80	No
MW80	80	60	Yes

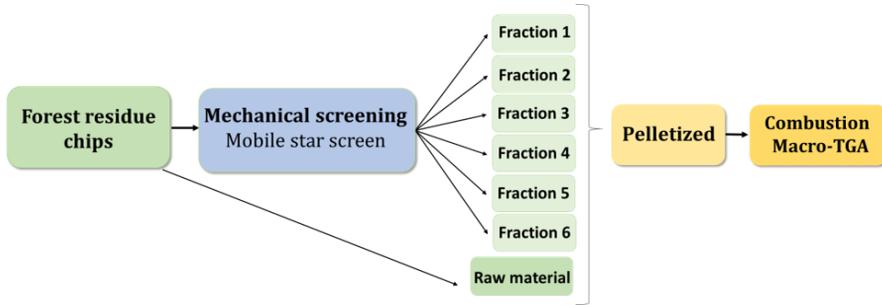


Figure 5. Schematic overview of the workflow in paper II.

In paper III, the combustion characteristics of barley straw that was pre-treated and stored with  $\text{CaCO}_3$  as a fuel design measure were empirically evaluated. The two investigated  $\text{CaCO}_3$  additivation levels of 2 and 4 w/w% were based on a novel approach to simultaneously improving the storage and combustion properties of agricultural biomass suggested by Xiong et al. [40]. Furthermore, quartz and olivine were evaluated as bed materials to investigate interactions between fuel ash and bed material when using high Ca additives.

### 2.2.3 Bed material evaluation

Paper IV examined how bed material in fluidized beds could be chosen to mitigate operational problems due to bed agglomeration in the combustion of agricultural residues, where barley straw was selected as the model biomass. The bed materials quartz, K-feldspar, and olivine were chosen to represent commercially available products with significantly different chemical structures and compositions. The main purpose was to compare the resulting bed agglomeration characteristics and degree of layer formation and investigate to what extent the different bed materials interact with fuel ash from agricultural residues that typically contain high K, Si, and Ca levels. Specifically, the sensitivity of the different materials to interaction with the bed ash rich in K-silicates was of interest.

## 2.3 Combustion

### 2.3.1 Combustion equipment

The combustion systems used in studies included in this thesis were a laboratory macro-sample thermogravimetric analysis equipment (MTGA) and a bench-scale 5 kW<sub>th</sub> bubbling fluidized bed reactor (BFB) suitable for agglomeration studies. Both thermal conversion systems are located at Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå University.

#### 2.3.1.1 Macro-TGA

The single pellet thermogravimetric reactor (Macro-TGA) was used in paper II to combust pellets produced after the mechanical screening. The Macro-TGA used enabled studies on the devolatilization and char combustion rates, ash transformation reactions, ash chemical composition, and temperature dependence of a single pellet. The reactor consisted of a furnace with internal dimensions of 200x130x130 mm equipped with an analytical balance and a quenching tower separated by a sliding hatch from the furnace zone. Electrical wall heaters heat the furnace to the set operating temperature. A pneumatic cylinder underneath the reactor was used to lower and raise the furnace into position for combustion. A platinum mesh basket connected to an analytical balance with a resolution of 1 µg was used as a sample holder. The pre-heated dry air was supplied to the furnace from the bottom of the furnace. A window on the front of the furnace allowed visual observation of the burning pellets. After complete combustion, the residual ashes were weighed. A schematic image of the reactor is presented in Figure 6.

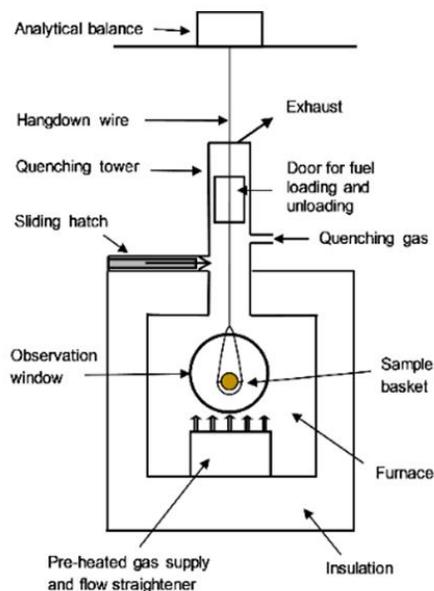


Figure 6. Schematic overview of the Macro-TGA used in paper II. Reprinted with permission from Bozaghian *et al* [124], copyright 2020 ACS.

### 2.3.1.2 Bubbling Fluidized Bed

The 5 kW<sub>th</sub> BFB with a total height of 2 meters with a bed and freeboard inner diameter of 100 mm and 200 mm, respectively, was used in papers III and IV. The bed consisted of 540 grams of sieved ( $200 \leq d \leq 250 \mu\text{m}$ ) bed material. The reactor was fitted with an electrical wall heating system to ensure even process temperatures during experiments. The temperature and the differential pressure in the top and bottom parts of the bubbling sand bed were measured to ensure that the bed was bubbling and determine the defluidization temperatures. A schematic image of the BFB reactor is presented in Figure 7.

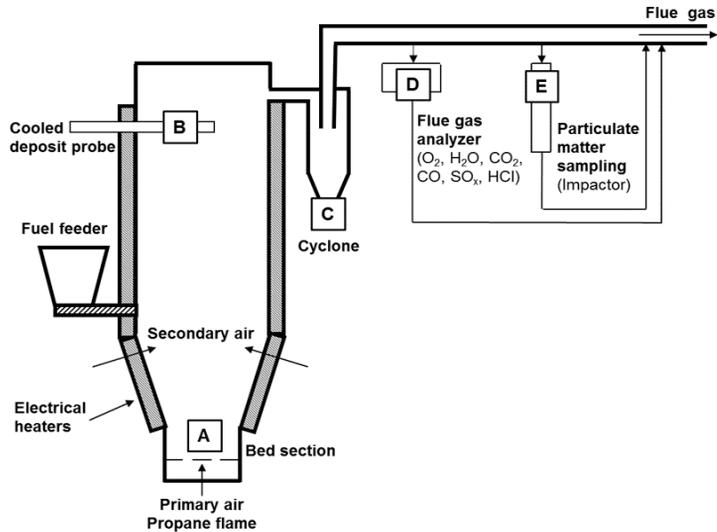


Figure 7. Schematic overview of the BFB reactor used in papers III and IV adapted from Skoglund *et al.* [125] with sampling points indicated: (A) bed ash, (B) deposition probe, (C) cyclone ash, (D) flue gas composition, (E) particulate matter. Reprinted with permission from Bozaghian *et al* [126], copyright 2018 Elsevier.

In papers III and IV, approximately  $\sim 0.5$  kg/hour kg of each fuel assortment was combusted separately in 540 g of bed material at  $700\text{ }^{\circ}\text{C}$  with a target combustion duration of 8 hours. If defluidization did not occur within the experimental time of 8 hours, a controlled agglomeration test was initiated following the method described by Öhman and Nordin [127]. This was achieved by increasing the bed temperature (with electrical wall heaters) at a  $2\text{ }^{\circ}\text{C}/\text{min}$  rate in a combustion atmosphere provided by a propane flame below the air distribution plate.

Samples were collected from the different stages in the biomass combustion process to evaluate the outcome of  $\text{CaCO}_3$  additivation to mitigate ash-related operational problems (paper III) and the process adaptation by different bed materials (paper IV). The samples collected are presented in the order of moving downstream in the combustion process, i.e., bed material samples, fly ash and PM, deposits, and gaseous components. The bed material samples were collected before (bed ash and bed material) and after (formed agglomerates) the agglomeration tests (sampling point A,

Figure 7). A deposit probe fitted with a removable steel ring was used to simulate a super heater surface on which deposits formed (sampling point B, Figure 7). The deposition probe ring was internally cooled to  $\sim 450$  °C and inserted into the flue gas stream. The deposition probe ring was carefully removed from the BFB reactor, and deposits formed were brushed off from the probe ring for analysis. The fly ash samples were collected from the cyclone (sampling point C, Figure 7) using a 13-stages Dekati® low-pressure cascade impactor for size-fractionated particulate matter (sampling point E, Figure 7). The fly ash samples collected from the cyclone had a cut-off diameter of  $\sim 10$   $\mu\text{m}$ , and based on particle diameters, samples from the impactor were divided into fine mode and coarse mode fractions. Online measurements with a Gaset DX-4000 Fourier-transformed infrared spectroscopy (FTIR) equipped with a zirconia cell for O<sub>2</sub> analysis (sampling point D, Figure 7) were used for the flue gas compositions reported in paper III.

## 2.4 Chemical analysis and characterization

The chemical analysis and characterization methods presented in the papers in this thesis span a variety of different analytical and characterization methods. Chemical characterization was only performed on residual ash samples collected after combustion experiments. The specific analysis and characterization methods used in the individual papers (I-IV) are summarized in Table 2.

### 2.4.1 Fuel characteristics

For moisture content determination (papers I- IV), samples were oven-dried at 105 °C overnight according to standard (Table 2). The dried samples were then milled to 1 mm for subsequent determination of ash content (papers I- IV), pH-value (paper I), and calorific value (paper II) according to standards (Table 2).

Samples for wood polymer composition analysis (paper I) for glucose, xylose, mannose, arabinose, galactose, rhamnose, Klason lignin, and acid-soluble lignin (ASL) were first dried at 40 °C for 48 h and then milled before the analysis was carried out by Celignis Analytical Laboratory. The samples for DNA-sequencing (paper I) were first freeze-dried and later homogenized by milling with liquid nitrogen before analysis. The DNA extraction and

amplification of samples were later performed by a genome sequencing company, Novogene sequencing (Table 2).

Standard fuel analyses were performed in papers II-IV according to standards for main ash-forming elements, sulphur, chlorine, volatile elemental composition (C, H, N), and oxygen (O) before the combustion experiments (Table 2). Details regarding the specific analyses can be found in the respective paper.

#### 2.4.2 Chemical characterization

All ash samples collected from the different stages in the combustion processes were analysed for morphology and elemental analysis using scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectroscopy (EDS). In addition, in papers II and III, the determination of crystalline compounds was also performed by powder X-ray diffraction (XRD).

The bed samples collected in papers III and IV were first sieved to separate bed ash particles and agglomerates from bed material, then moulded in epoxy resin and polished to ensure a smooth surface before the chemical characterization with SEM-EDS. The powder samples collected in papers II and III (bottom ash samples in paper II and fly ash samples from the deposition probe ring, cyclone, and size-fractionated PM in paper III) were mounted on double-sided carbon tape before being subjected to XRD and SEM-EDS analysis.

##### 2.4.2.1 SEM-EDS

The morphology and elemental composition of ash samples collected after the combustion experiments were analysed with SEM-EDS. The results in papers II-IV were obtained using a Carl Zeiss EVO-LS15 equipped with an Oxford X-Max EDS detector located at TEC-lab, Umeå University. The SEM-EDS was operated at acceleration currents between 15-20 kV with a probe current of 400-500 pA. Backscattered electron (BSE) images were obtained in the SEM, and with the energy dispersive X-ray spectroscope (EDS), the elemental composition corresponding to the BSE images was obtained as the EDS technique identifies elements and their relative proportions (i.e., atomic %) with C and O excluded due to their prevalence in the sample mounting material.

Powder samples of residual ash (paper II) and fly ash collected from cyclone ash, deposition probe rings, and size fraction particulate matter (paper III) were transferred to double-sided carbon tape. In contrast, bed samples collected before and after agglomeration (paper III and IV) were moulded in epoxy resin and polished to ensure a smooth surface of individual cross-sections of bed particles before analysis. This permitted evaluation of how bed ash and bed particles interact including the formation and chemical composition of layers or agglomerate necks.

Typical elements included in the EDS analysis were K, Na, Ca, Mg, Fe, Al, Si, P, S, and Cl. It should be noted that C and O were excluded due to their presence in both carbon tape and epoxy resin prohibiting a reliable analysis of these two elements. Depending on the purpose of the analysis, the SEM-EDS analysis methodology was adapted and included area analysis, spot analysis, line scans, and mapping.

#### 2.4.2.2 Powder XRD

Powder X-ray diffraction (XRD) analysis was performed on a Bruker D8Advance with CuK $\alpha$ -radiation fitted with a Våntec-1 detector located at Tec-lab, Umeå University, for crystalline content in papers III and IV. The software Diffrac.EVA (Bruker-AXS GmbH, Germany) equipped with ICSD PDF-2 [128] database was used to qualitatively analyze the samples, and later, Rietveld refinement in TOPAS 4.2 (Bruker-AXS GmbH, Germany) was used for semi-qualitative analysis of relative concentrations of compounds, using .cif files for the identified compounds obtained from ICSD-Web.

The analyses were performed using two types of sample holders; large-volume samples (cyclone ash and bottom ash) were mounted in plastic holders while samples with small amounts were mounted on silicon crystal low-background sample holders. Analyses were made with sample rotation using  $\theta$ - $\theta$  mode in the range of 10° - 70° and continuous scans, where collected diffractograms were cumulatively added. Data were collected until peaks were sufficiently defined to admit identification.



### 3. Results

#### 3.1 Storage-induced changes in bark - paper I

The temperatures at the top (T) and the side (S) of the bark pile increased rapidly. They reached their maxima around day 15 (62 and 48 °C, respectively); thereafter, the temperature at the top stabilized and slowly declined while the shape of the side temperature curve started to show similarities to the ambient temperature (Figure 8). The temperatures at the bottom and in the center of the pile gradually increased throughout the storage period. Unfortunately, the thermocouple at point C malfunctioned during the trial period. It is possible that the two temperatures B and C (Figure 8) would have converged, provided both measurements would have been available for the entire storage period. The temperature in the center can therefore be assumed in the region of 50 to 60°C at the end of storage.

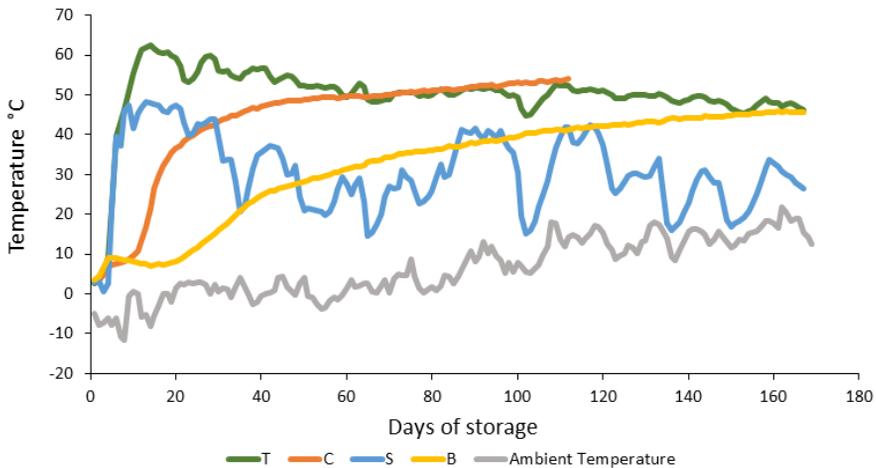


Figure 8. Monitored temperatures at the cross-section for week 24. Temperature (°C) vs. time (days) at the top (T), center (C), side (S), and bottom (B) during 24 weeks of storage.

Analysis of bark properties indicated that the most significant changes over time were observed near the pile surfaces (on the side and top) (Figure 9). The top sample from week 24 differed the most from the other samples – having the highest moisture content, ash content, pH value, and lignin content and lowest arabinan, galactan, and rhamnan concentrations. The bark

properties in samples from the pile's center (C) seemed relatively unchanged over time, as no significant ( $p>0.05$ ) differences were observed over time. Furthermore, the genome sequencing showed that the Ascomycetes fungi were the predominant flora in large parts of the pile during the storage of which Eurotiomycetes and Sordariomycetes were the dominating classes.

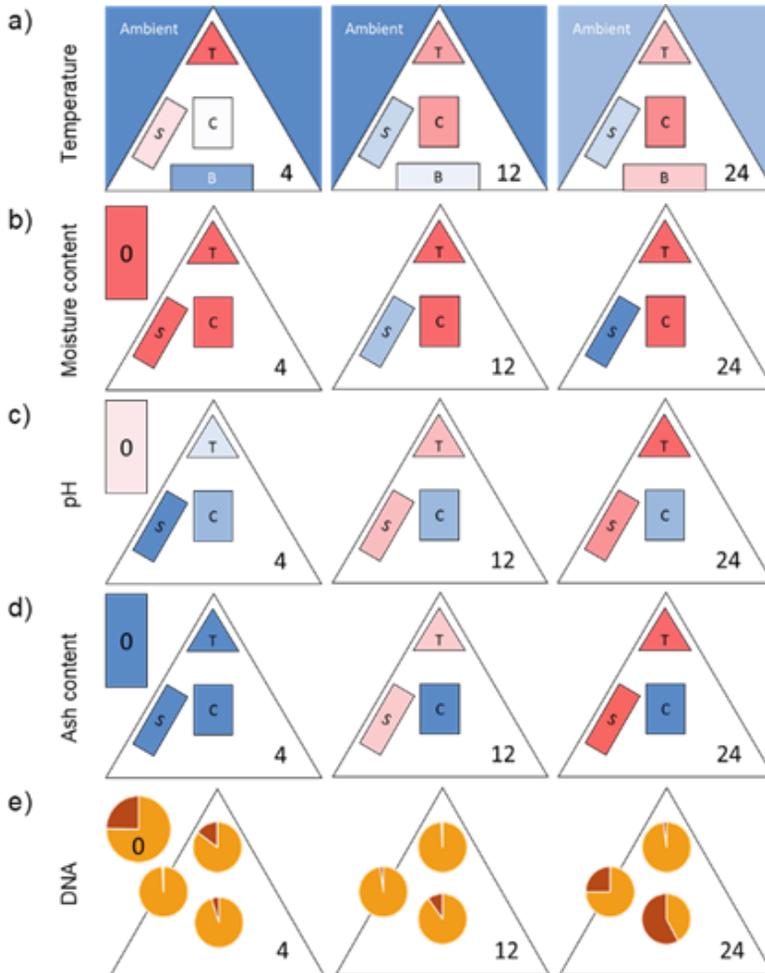


Figure 9. Illustration of the conditions in the bark pile after 0, 4, 12, and 24 weeks of storage. a) Temperature (range: 2 to 57 °C), b) moisture content (range: 34 to 61 %), c) pH (range: 3.3 to 4.4), d) ash content (range: 3.1 to 3.9) are colored from the lowest (blue) to the highest (red) value, e) share of the number of species in the Ascomycetes (yellow) and Basidiomycetes (brown) fungi divisions, based on the DNA analysis.

The dense grouping of the samples from the pile's center (C4, C12, and C24) in the PCA model (see Figure 10) indicates minor changes in bark properties in the middle of the pile. However, more changes occur during storage on the side, and especially at the top, with increasing ash content and pH value and decreasing arabinan, galactan, and rhamnan.

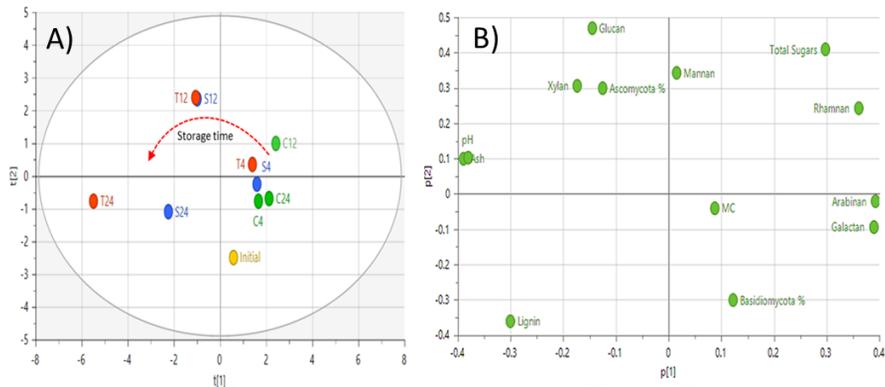


Figure 10. Results of PCA analysis of effects of storage time on bark properties. A) score plot colored by sample locations and B) loading plot with measured responses.

## 3.2 Fuel design measures

### 3.2.1 Mechanical screening - paper II

In paper II, mechanical screening as a fuel design concept resulted in a decrease in ash content, fine particles, and moisture content, which increased the higher heating value (HHV). Of all the tested star screen settings, the setting with the lowest rotational speed and with a windshifter (MW80) showed the greatest reduction in ash content (-7.4%), fine particles (-23%), and moisture content (-3.9%). However, correlations between ash content and fuel mass loss (% wet basis) (Figure 11) showed significant mass losses (20-50 wt%) as a result of screening, especially at the MW80 setting (lowest rotational speed and with windshifter). Despite screening and windshifting, significant amounts of fine particles were still left in the screened forest fuel chips (accept fractions).

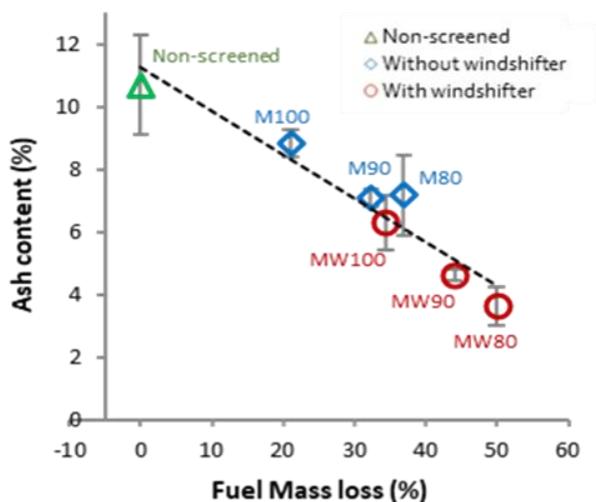


Figure 11. Quantified effects of the different mechanical screening settings showing ash content vs fuel mass loss (%) during screening of the forest residue chips. Reprinted with permission from Bozaghian *et al* [124], copyright 2020 ACS.

The amount of main ash-forming elements (mg/kg dry basis) in the fuels decreased by screening, with the most significant reduction for Si and Al, irrespective of the screening procedure. This indicates that screening selectively removes sand and soil inclusions more than ash-forming elements in the biomass. Despite screening, the dominating elements in all fuels (non-screened and screened) were Si, Ca, K, and Al. The relative ash composition, on molar basis (normalized to total ash-forming elements), did, however, not change considerably after screening. Reduction of Si, when extrinsic Si was removed by screening, increased the relative concentrations of primarily Ca and K proportionally; apart from this, only minor changes in fuel ash composition were achieved by screening.

The ash composition of the fuels, presented as weight-% of oxides, was used in a composition diagram consisting of  $K_2O + Na_2O$ ,  $CaO + MgO$ , and  $SiO_2$  to predict slagging tendencies based on sintering category in biomass combustion for biofuels poor in P (Figure 12) [129]. All fuels (non-screened and screened) have composition resulting in the higher slagging potential (black-colored area = major slagging tendency), despite the shift in the compositional diagram due to removal of Si (and corresponding relative increase of both Ca and K) in MW90 and MW80. Consequently, the

mechanical screening for this fuel cannot be expected to change combustion characteristics and ash melting behavior except by reducing the absolute amount of ash introduced in the combustion process. Furthermore, no significant deviation between the screened and non-screened fuels could be observed during the laboratory single pellet combustion tests.

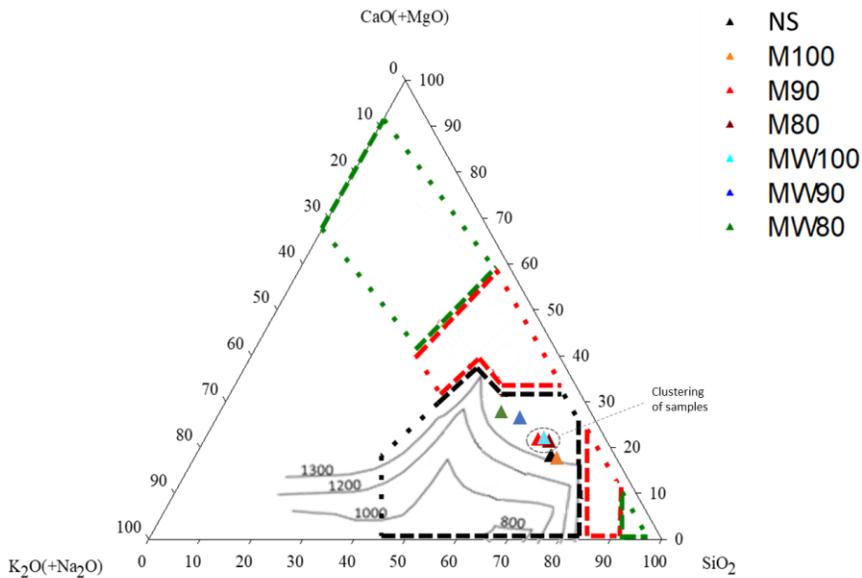


Figure 12. Fuel ash composition of screened and non-screened forest residue chips before combustion in the  $\text{SiO}_2$ - $\text{K}_2\text{O}(\text{Na}_2\text{O})$ - $\text{CaO}(\text{MgO})$  system. Colored areas corresponds to green = no/low slagging tendency, red = moderate slagging tendency, and black = major slagging tendency. Reprinted with permission from Bozaghian *et al* [124], copyright 2020 ACS.

### 3.2.2 $\text{CaCO}_3$ additive - paper III

As a result of increased Ca content (2% and 4%  $\text{CaCO}_3$ ) in paper III, the melting temperatures of the formed slag increased significantly, indicated by increased defluidization temperatures for both quartz and olivine (Table 4). The defluidization temperatures for the olivine bed material were well above normal bed temperatures in FB biomass boilers (800-900 °C).

Table 4. Defluidization temperatures for the different fuel mixes and bed materials.

	0% quartz	0% olivine	2% quartz	2% Olivine	4% quartz	4% olivine
T °C	854	860	912	900	920	>1000

The SEM area analysis showed that the concentration of Ca increased at the same time as K remained at the same concentration suggesting that Ca-additive reacts with the formed K-silicate melts as expected. However, the emissions, particularly the amount of KCl (in the deposits and fine particulate matter) (Figure 13) and CO in the flue gas, increased with CaCO<sub>3</sub> addition for both bed materials, even though the O<sub>2</sub> concentration was kept at 10-14% during all times (Figure 14).

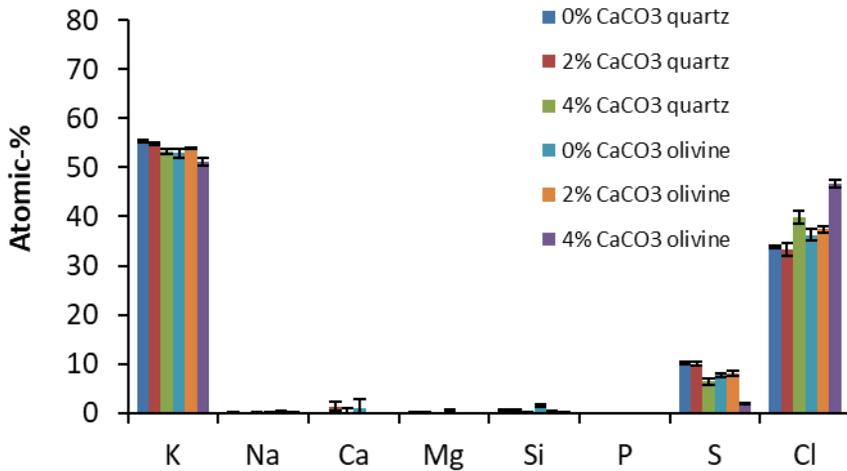


Figure 13. Elemental composition on C-, O-, Fe-, and Al free basis of fine mode fractions of the particulate found in all combusted fuels. Reprinted with permission from Bozaghian *et al* [126], copyright 2018 Elsevier.

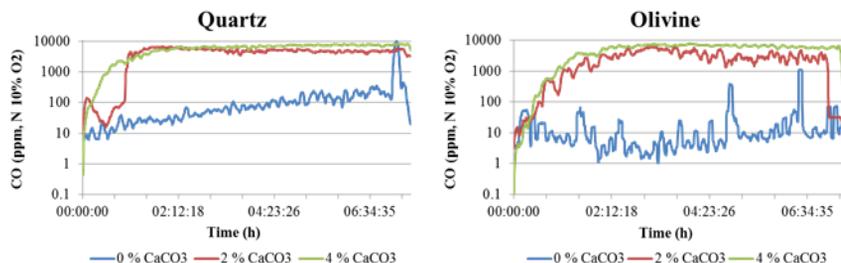


Figure 14. CO concentrations during combustion normalized to 10% O<sub>2</sub> dry gas for quartz bed and olivine bed. Reprinted with permission from Bozaghian *et al* [126], copyright 2018 Elsevier.

### 3.3 Process adaptation – bed materials – paper IV

The three bed materials displayed different interaction types with the bed ash formed by barley straw. Quartz displayed layer formation according to mechanisms previously observed for straw biomass, but the relatively high Ca content made the continuous operation possible for the combustion period duration of eight hours. K-feldspar performed the worst with rapid agglomeration after less than two hours of operation at low temperatures. Olivine displayed a higher initial defluidization temperature than quartz, suggesting that for only eight hours of combustion the bed ash composition is the main factor for agglomeration in these experiments. The resulting bed agglomeration temperatures for the respective bed materials are provided in Table 5.

Table 5. Initial defluidization temperatures for quartz, K-feldspar, and olivine in bubbling fluidized bed combustion of barley straw.

	Quartz	K-feldspar	Olivine
Temperature °C	780	730	815

Typical bed layers and agglomerates formed during the combustion of barley straw with the bed materials are shown in Figure 15. During the combustion of straw with quartz, continuous thin layers (3-5 μm) rich in K were found on quartz bed particles before and after agglomeration. Indications of inner and outer layers were only observed on quartz bed particles after the agglomeration test. The formed inner layer consisted mainly of K, whereas

the formed outer layer consisted of Ca. An overview of the bed sample showed a large number of agglomerates where the quartz bed particles, with continuous thin layer formations rich in K and Ca, were joined by thick necks rich in K, Ca, and Si. The chemical composition of the sieved samples of ash particles, melts, and agglomerate necks showed an increased amount of K and Ca and a decreased amount of Si for all samples.

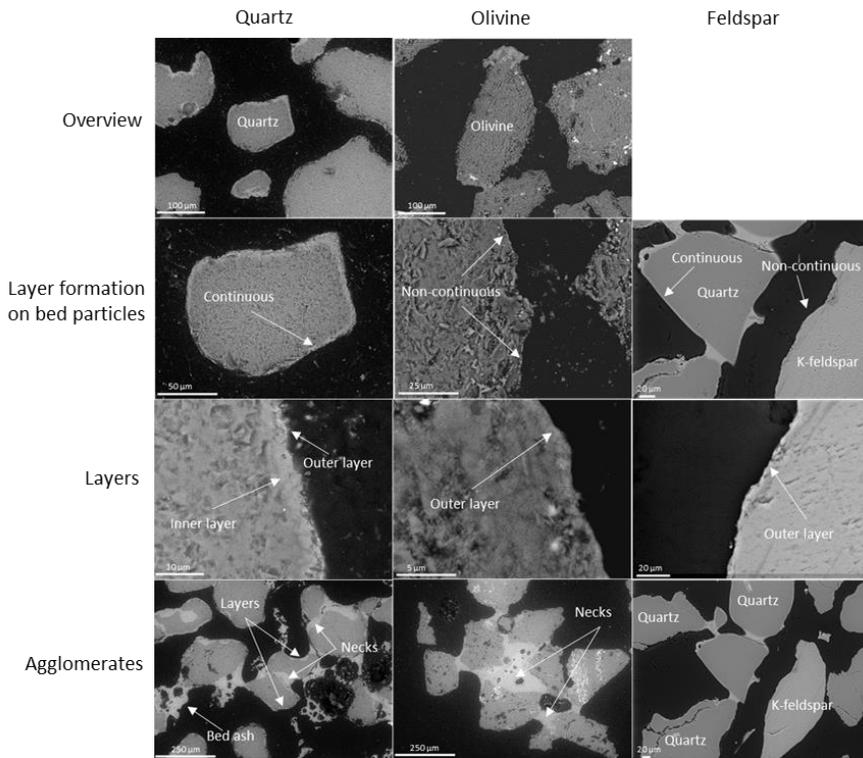


Figure 15. Typical overview, bed layer formation, and agglomerates from combustion of barley straw with quartz, olivine, and feldspar bed materials.

For the feldspar case, the bed defluidised within 2 hours of combustion, and thus, no sample could be collected before agglomeration. An overview showed that the layer formation was scarce on the feldspar bed particles after agglomeration. The observed layers were very thin consisting mostly of Ca. However, bed layer formation was detected on quartz particles present as contaminants in the feldspar bed material. The layer formation on quartz was very similar to that described in the quartz case, with continuous thin layers rich in K and Ca. The formed agglomerates in the feldspar bed consisted of

different bed particles (feldspar and quartz). Furthermore, the agglomerates showed that the neck's composition varied according to the adjacent grains (feldspar and quartz). In cases where Na-feldspar was incorporated in the agglomerates, an increase of Na was observed. However, most of the agglomerates found consisted of quartz particles with continuous thin layer formations rich in K and Ca joint by K-Ca-rich necks. No significant difference in chemical composition between melts and agglomerate necks could be detected in the feldspar case, except for an increase in Ca in the agglomerate necks.

The formation of layers on olivine bed particles before and after agglomeration was scarce. The observed layers were thin and discontinuous (3 to 5  $\mu\text{m}$ ), consisting almost exclusively of K, but small amounts of Ca were detected in some layers after agglomeration. No clear indications of an inner and outer layer were observed for olivine bed particles. The formed agglomerates observed had no significant bed layers on the olive bed particles. However, the necks were rich in Si, Mg, K, and Ca. Furthermore, no significant differences in chemical composition between samples of ash particles, melts, and agglomerate necks could be detected. This confirmed that bed ash composition is mainly responsible for defluidization. However, compared to the fuel ash composition, an increase in Mg was observed in all samples indicating that the olivine bed material may deteriorate over time.





## 4.1 Storage-induced changes in bark

The rapid temperature increase on the side and top (Figure 8 and Figure 9a) may be due to chemical and biological processes. It can be assumed that the freshly cut bark had high levels of accessible sugars and many living parenchymal cells [43]. Furthermore, exposure to ambient air at the top and side created suitable conditions for microbial degradation and respiration. Both are exothermal processes [43, 51, 130, 131], explaining the rapid temperature increase for the locations near the surfaces (S and T). Based on the same reasoning, the delayed temperature increase in the pile's center compared to the top and side may be due to the lack of contact with ambient air. However, the temperature in the pile center gradually increased and is assumed to be in the range of 50 to 60 °C at the end of storage. However, the maximum temperatures on the side and top were reached on day 15; after that, the temperature decreased (on the side) or stabilized (at the top), probably as a result of the heat required for evaporation of water (drying) or low levels of thermophilic microorganisms that can tolerate high temperatures. Furthermore, the rapid temperature increase observed on the side and top of the bark pile can lead to the evaporation of compounds, such as CO<sub>2</sub>, CO, and CH<sub>4</sub>, and a decrease in valuable extractive substances from the lignocellulosic matrix [43, 132, 133].

The analytical results show that most significant ( $p < 0.05$ ) changes in moisture content, ash content, pH value, lignin content (Figure 9a-c), and the relative concentration of individual sugars occurred near the pile surfaces. The bark in the pile's center was primarily unchanged. Although no significant ( $p < 0.05$ ) changes in total sugar content were observed between the locations (S, C, and T) over time, the increased ash and lignin content at the top from week 24 indicates biomass loss. The increase in lignin content and the decrease of the relative concentrations of arabinan, galactan, and rhamnan indicate changes in the lignocellulosic matrix. Aside from this, the results show only minor or no changes in bark material properties from the pile center during the first twelve weeks of storage for the side and top locations. Consequently, the bulk of the stored material was primarily unaffected. However, the genome sequencing results indicate high concentrations of Eurotiomycetes and Sordariomycetes fungi in large parts

of the bark pile, which can pose major health risks when handled. These classes include several known molds that are pathogens, such as *Penicillium*, *Aspergillus* (class of Eurotiomycetes) and *Trichoderma*, (class of Sordariomycetes) [45, 51, 134]. Exposure to high concentrations of these fungal spores can lead to health problems and should therefore be avoided [134].

The indicated storage-induced differences in macromolecular composition between locations in the pile (Figure 10) should be further investigated. According to measured properties and predictions from the PCA model (Figure 10), material from the top will have higher ash, lignin, and xylan content and lower total sugar content than from other locations in the pile, making it less suitable as raw material for biorefining, e.g. ethanol production, but better as a value-added raw material for, e.g. lignin-based products. This interesting observation can contribute knowledge for more efficient use of resources for processing biomass into suitable fuels or value-added products.

The ash composition of the bark samples, presented as weight-% of oxides, in a compositional diagram of  $K_2O + Na_2O$ ,  $CaO + MgO$ , and  $SiO_2$ , indicates negligible changes during storage (Figure 16). The results suggest that the combustion characteristics of the stored bark will not change during storage.

This study shows that the most significant changes were observed near the pile surfaces, where changes in the lignocellulosic matrix were observed. However, these changes will not affect the combustion characteristics of the stored bark except in cases where processes are sensitive to amounts of ash rather than their slagging behaviour but may affect other processes that utilize different components of the lignocellulosic matrix.

## 4.2 Fuel design measures

### 4.2.1 Mechanical screening

The results obtained from the screening study highlight that the fuel ash content is a poor indicator for ash-related operational problems induced by melt formation in the ash. To mitigate ash-related problems understanding the underlying ash chemistry is important. Screening efficiently reduced the

amount of ash and fines but was associated with significant fuel mass losses (20-50%); in addition, screening also entails additional machine costs. However, despite the reduction in ash content (Figure 11), only minor changes in fuel ash composition were achieved by screening. Fuel analysis indicated that the main ash-forming elements in all fuels, based on molar ratios, were K, Ca, and Si. K and Ca-silicates will therefore dominate the ash transformation reactions despite screening. The overall composition of the fuel ash affects the melting point of the bottom ash; the melting point will decrease if alkali is abundant as it reacts with silicates forming low-melting alkali-silicates. On the contrary surplus of alkaline earth metals, primarily Ca, will increase the melting point of the bottom ash. Furthermore, based on the compositional diagram, all fuels have a composition (K(+Na), Ca(+Mg), and Si), resulting in a higher slagging potential (Figure 12), indicating that screening had limited value for changing the dominant ash transformation chemistry.

Depending on the overall composition of the fuel ash, the melting point of the bottom ash can vary by several hundred degrees. If alkali is abundant, it can react with the silicates, and the melting point will decrease. Therefore, ash content alone may not be sufficient as an indicator to predict ash-related operational problems. Understanding the underlying ash chemistry is more important for handling different fuels. Furthermore, the burner technology strongly influences the amount of slag formed during combustion [99]. Large-scale plants are more tolerant to different fuels and the amount of ash introduced as they are often equipped with ash handling systems. These plants are not sensitive to the amount of ash formed, as the ash can be continuously discharged if the ash is unproblematic, i.e. low amounts of alkali. On the other hand, small and medium-scale plants are rarely equipped with more than a cyclone for flue gas cleaning, making the ash content and composition more crucial. In these cases, screening can be an alternative to improving the fuel quality, but the economic aspects of additional machine costs must also be considered.

#### 4.2.2 CaCO<sub>3</sub> additive

The CaCO<sub>3</sub> addition had both positive and negative effects on the combustion characteristics of straw. Adding CaCO<sub>3</sub> resulted in the formation of Ca-rich silicates with higher melting temperatures which significantly increased the total defluidization temperatures for both quartz and olivine

(Table 4). The incorporation of Ca (as  $\text{Ca}^{2+}$ ) into low melting K-silicates fits well with other studies where Ca addition has been used with Si-rich biomass [95, 96, 104]. The morphology of the bed ash particles and the entrained Ca-compounds downstream in the flue gases suggests that 2% additive is primarily consumed by reactions with silicates in the bed. In contrast, the 4% additive level exceeds the amount required for reacting with available sites in the silicate matrix, as indicated by the excess  $\text{CaCO}_3$  remaining in the bed ash or CaO in fly ash.

However, regardless of fuel blend or bed material, the deposits and particulate matter increased due to Ca-addition, which is likely related to increased gaseous alkali compounds that condensate further downstream. The deposits and particulate matter were dominated by KCl (Figure 13), which suggests a potentially elevated risk for alkali chloride-induced corrosion. Flue gas composition also showed adverse effects of the Ca-additive as elevated CO concentrations were observed (Figure 14). The elevated CO concentrations are believed to be related to Ca-addition and the release of surplus K to the gas phase, which interferes with the oxidation of  $\text{CO}_2$ . Furthermore, an interesting observation is the gradually increased CO concentration during combustion of barley straw with no additive in the quartz case. The CO concentration increased 10 times (from 10 ppm to 100 ppm) during the 8 hours of combustion. This may indicate that continuous combustion of alkali-rich biomass may be problematic regarding the increased KCl and CO as the quartz particles may lose their alkali buffering effect; thus, more K can be released into the gas phase. This observation may be important and relevant for the use of quartz as bed material in the combustion of alkali-rich biomass, thus must be studied further. However, this effect was not observed in the olivine case with no Ca-additive.

This study shows that the use of additives in this case to mitigate alkali-induced ash-related problems is a balancing act between retaining the alkali in bottom ash or releasing it into the flue gas as emitted particles or volatile species. Therefore ash transformation reactions in bed and bottom ash should be considered alongside reactions in the flue gas. The suggested Ca-additive levels (especially 4%) in this study may be an issue for combustion, possibly good from a gasification perspective where the increased Ca leads to enhanced catalytic activity for tar decomposition. Furthermore, the cost of  $\text{CaCO}_3$  additive must also be taken into account.

However, from an operational perspective, the results suggest that further amendments at the combustion site would be required for the successful combustion of agricultural biomass stored with high amounts of Ca-additives due to the high KCl and CO concentrations observed. Additives such as kaolin, commonly used to reduce gaseous alkali compounds, could possibly be employed to address the issues identified in this study. Therefore Ca-addition to alkali-rich biomass should consider more process parameters than the slagging behaviour of the ash, where it has a beneficial effect.

### 4.3 Bed material adaptation

The observations of layer formations and agglomeration involving quartz, natural feldspar, and olivine material from the combustion of barley straw clearly show different accumulations of fuel ash on the surface of the studied bed particles as well as different layer formation mechanisms (Figure 15). This is likely related to the polymerization of silicates-based bed materials where quartz has a high degree of polymerization, feldspar with a lower polymerization degree than quartz, and olivine is completely depolymerized.

The combustion of barley straw with quartz shows that the fuel ash interaction with quartz bed particles follows the proposed layer-forming mechanism [70, 80, 115, 135, 136], suggesting that alkali compounds from the fuel interact with the bed material under the formation of alkali-rich layers (continuous inner layers) (Figure 15). It has been suggested that these inner layers provide a sticky surface onto which other bed particles or ash particles can stick. The thin continuous layers of mainly K on a majority of analysed quartz bed particles clearly show that the proposed mechanism is initiated and detected. The indication of an outer layer consisting of Ca observed after agglomeration indicate a gradual accumulation of fuel ash Ca occurring on the sticky K-rich inner layers, further supporting the proposed mechanism, suggesting the formation of an outer layer (by adhering of ash particles) or Ca gradient in the inner layer. The mechanisms have been shown to be time and temperature-dependent [137]. The relatively short experiments (8 hours) can explain the lack of significant differences in layer thickness before and after agglomeration and the few Ca-rich outer layers observed. The layers observed on bed particles incorporated in agglomerates were thicker, but this might very well be the result of the close proximity to

molten fuel ash. The composition of fuel ash and melt was very similar in all quartz samples, indicating that the layer formation depends on time and temperature. The high amount of agglomerates found in the quartz bed compared to the corresponding olivine and feldspar beds suggests high interaction between fuel ash and quartz bed particles.

The feldspar experiments caused early bed defluidization already after ~2 hours of operation at temperature of ~730 °C. Despite this, feldspar bed particles only showed a low tendency for layer formation as layer formation on feldspar particles was scarce, indicating low interaction between feldspar bed particles and fuel ash. This is in agreement with previous work focusing on woody-type biomass [120, 138]. Although inclusions of Ca on a few feldspar particles were observed, layer formation on the quartz, present as contaminations in the bed material, was more comprehensive in comparison (Figure 15). The layer formation on the quartz particles was similar to that described above, with continuous thin layers of K and Ca. The accelerated layer growth on quartz compared may be partially caused by the low degree of interaction of feldspar particles with bed ash, increasing the reaction rates with the quartz particles present while also removing Ca which could have improved stability of layers on quartz.

The formed agglomerates in the feldspar bed showed varying chemical composition in the necks according to adjacent bed particles. A proposed mechanism is the diffusion of K and Na out of the K-feldspar and Na-feldspar, respectively, into the necks. The results show an increase of Na in necks in cases where Na-feldspar was incorporated in the agglomerates. Since K and Na can be expected to have similar properties [13, 67], it can be assumed that also K will diffuse into fuel ash if the composition favours it [108, 109, 139]. This diffusion of alkali (K and Na) out of feldspar particles potentially increases the amount of alkali available for reaction in the bed compared to both the quartz and olivine cases. Increased alkali typically implicates the formation of low melting alkali silicates and reduction in defluidization temperatures. This is further supported by the low agglomeration temperature in the feldspar experiment. Despite the diffusion of alkali out of feldspar particles, K-feldspar has been shown to perform well under gasification or combustion conditions of woody-type biomass or phosphorus-rich residues [108, 109, 139-143], probably due to an already favourable overall fuel ash composition. The feasibility of feldspar as an alternative bed material during the combustion of alkali-rich lignocellulosic

residues should not be discarded, but the enhanced risk of extensive interaction with quartz commonly included in feldspars should be carefully considered.

During the combustion of barley straw with olivine, before and after agglomeration, very few bed particles with formed layers were observed (Figure 15), suggesting limited interaction between fuel ash and olivine particles. The layers identified were thin (3-5  $\mu\text{m}$ ) and discontinuous. This observation indicates that olivine is less susceptible to alkali-induced layer formation than quartz, as previously suggested [116, 118, 119]. The significant increase of Mg observed in the ash and melt of all samples indicates that a substitution reaction between Ca, introduced with the fuel, and Mg in the bed particles, is taking place, or possibly Mg migrates from the olivine bed material to the melt.

The results from this barley straw study suggest that for alkali-rich fuels, olivine displayed the best process performance and feldspar the worst of the bed materials tested. The key parameter was how the silicate matrix of the bed material interacts with alkali, and the resulting properties of layers. The feldspars do have a risk of alkali migration to fuel ash or surrounding quartz particles, whereas the overall fuel ash properties are more important when olivine is used as a bed material. This is based on the degree of polymerization in the silicate matrix, with quartz reacts fastest with alkali.

#### 4.4 Practical implications

The results in this thesis emphasize the importance of fuel ash composition from a combustion perspective. As the combustion characteristics of the bark did not change during storage, it may suggest that for bark intended for thermal conversion, the cheapest storage solution that does not imply major loss of energy carriers or a higher risk for self-ignition should be implemented.

The ash transformation reactions that take place during thermal conversion are in many aspects similar regardless of combustion technique or size of the thermal conversion process; however, larger plants often have appropriate ash-handling systems compared to smaller plants and are, therefore, more robust. Irrespective of the plant size, measures taken to improve the combustion properties of fuels must be cost-beneficial. Even if

the ash content of the fuel is improved by screening, as demonstrated in paper II, screening implies substantial biomass losses. It may not improve the combustion characteristics of the screened fuels. Screening may not be recommended in cases where the plant is equipped with ash handling systems or if the purpose of screening is to improve ash-related operational problems. Ca-additivation efficiently reduced the slagging tendencies during the combustion of barley straw by altering the fuel ash composition. However, the additive must be applied appropriately (based on the fuel ash composition) to avoid additional problems such as corrosion and elevated CO(g) concentrations in the flue gases.

The importance of choosing appropriate bed material during fluidized bed combustion of lignocellulosic residues rich in K is emphasized in paper IV. Feldspar and olivine both showed low interactions with the fuel ash. Despite the low interactions between fuel ash and feldspar particles, alkali diffusion out of feldspar may potentially increase the amount of alkali in the bed. Using feldspar as bed material during combustion of lignocellulosic residue rich in K should be considered. The olivine bed material displayed a better performance during the combustion of barley straw with low interactions with the fuel ash. It is possible that similar neosilicates such as  $\text{CaSiO}_4$  could also display properties suitable for agricultural residues since they would have similar reaction pathways with the bed ash.



## 5. Conclusions

The results and experiences presented in this thesis contribute to increased knowledge of the impact of storage and fuel design and process adaptation measures during the combustion of lignocellulosic residues and their relevance and consequences for mitigating ash-related operational problems. In general, it was found that process performance is related to the actual chemical composition of the investigated residues rather than measures such as ash content reduction with regard to melting. The broad inclusion of lignocellulosic residues in the bioenergy system should therefore rely on fuel characterization concerning which ash forming elements are present, since ash content is a poor indicator of fuel quality with regards to slagging or agglomeration.

The combustion characteristics of lignocellulosic residues emphasize the importance of a good understanding of the mechanisms that govern the ash transformation reactions. The overall findings can be concluded as follows:

- The most significant changes in bark properties during storage were observed near the pile surfaces, where changes in the lignocellulosic matrix were observed. However, these changes will not affect the combustion characteristics of the stored bark but may affect other processes.
- Mechanical screening as a fuel design measure did not have an impact on ash transformation reactions, and hence, no significant changes in combustion characteristics can be expected by the screening.
- The  $\text{CaCO}_3$  additivition did impact the ash transformation reactions by reducing the amount of alkali in the bed; as a result, the defluidization temperature increased, but the increased volatilized alkali implies an elevated risk for the formation of corrosive compounds and CO concentrations. This demonstrates that additivition during storage could benefit the performance of lignocellulosic residues in thermal conversion but that further measures may be required.
- Bed ash from barley straw showed a high interaction between fuel ash and quartz bed particles, whereas low interactions between fuel

ash and olivine and feldspar bed particles were observed. The results suggest that bed materials with a depolymerized silicate matrix such as feldspar or olivine are less susceptible to reaction with alkali introduced with the fuel ash. However, diffusion of alkali out of feldspar grains potentially increases the amount of alkali in the bed compared to the quartz and olivine cases, resulting in a reduction in defluidization temperature. Therefore, fluidized bed conversion of lignocellulosic residues from agriculture that typically have a K-rich ash content may display a better process performance with olivine, provided that the fuel ash itself does not melt at too low temperatures.

## 6. Future research

The results regarding bark storage in paper I indicated storage-induced differences in macromolecular composition between locations in the pile that should be further investigated. This would increase the knowledge on biomass property changes during storage and potentially lead to more efficient use of biomass resources for other applications than thermal conversion. Furthermore, the bark storage did not seem to affect the ash chemistry despite the changes in the lignocellulosic matrix. Further studies are needed to evaluate the effect of storage on the combustion properties of bark stored in a large-scale industrial pile.

Further studies are also needed on alternative bed materials that have low interaction with fuel ash and do not contribute to the overall alkali in the bed during fluidized bed combustion of lignocellulosic residues rich in alkali. The observation regarding quartz particles' alkali buffering effect observed in paper III may also be further investigated as it may be important for using quartz as bed material in the combustion of alkali-rich lignocellulosic residues.



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## Popular science summary

Utilizing certain biomasses for bioenergy - especially from lignocellulosic residual streams from forestry and agriculture - is an important strategy for phasing-out fossil fuels to reduce CO<sub>2</sub> emissions while increasing sustainability in the energy sector. However, some challenges are associated with these residues during storage, handling, and combustion. During combustion, the chemical composition of the fuel can lead to the formation of unwanted compounds that can cause ash-related operational problems such as slag formation, corrosion, particulate emissions, or agglomeration of the bed sand material in fluidized bed boilers. To a great extent, these ash-related operational problems cause costly maintenance and, in worst case, cause unwanted shutdown of bioenergy processes.

With focus on increasing the use of biomass for bioenergy, this thesis has examined the effect of storage, fuel design, and process adaptation to improve the combustion properties of biomass residues. This was achieved by first studying property changes in bark during storage. Then, mechanical screening and addition of Ca were implemented as fuel design measures on forest and agricultural residues to change the chemical composition of the fuel. In addition, a process adaptation measure was studied in which the interactions between different bed materials and the fuel ash were evaluated during combustion in a bubbling fluidized bed, as an alternative in cases where fuel design measures are not desired or possible.

The overall results showed significant changes in main bark components in the bark pile's outer parts during storage; however, these changes are not expected to impact the combustion properties. The mechanical screening reduced the amount of ash in the fuel but resulted in significant biomass losses and did not change the ash chemistry to improve fuel conversion properties. The Ca addition increased the defluidization temperatures by

raising the melting temperatures of the ash. Still, the Ca-addition caused an increased risk of formation of corrosive compounds and led to high concentrations of carbon monoxide in the flue gases for both the quartz and olivine bed materials tested. Comparing the different bed materials during combustion in a bubbling fluidized bed showed high interactions between quartz particles and the fuel ash. In contrast, olivine and feldspar showed low interaction with the bed ash. Despite this, feldspar as a bed material when combusting fuels rich in alkali such as lignocellulosic residues from agriculture was found to be the least suitable of the bed materials tested. Alkali from feldspar particles diffused and thus increased the total amount of alkali in the bed, which means an increased risk of agglomeration. Overall it was found that if any measures are applied to improve the utilization of lignocellulosic residues in bioenergy applications, they should consider how the ash chemistry is affected to be worthwhile for improvement of performance in fuel conversion.

## Populärvetenskaplig sammanfattning

Bioenergi som avänder vissa typer av biomassa – särskilt lignocellulosiska restströmmar från skogs- och jordbruk – är en viktig strategi i arbetet med utfasningen av fossila bränslen för att minska CO<sub>2</sub>-utsläppen och samtidigt öka hållbarheten inom energisektorn. Det finns dock en del utmaningar förknippade med dessa restströmmar under lagring, hantering och förbränning. Under förbränning kan bränslets kemiska sammansättning leda till att oönskade föreningar bildas som kan orsaka askrelaterade driftsproblem såsom slaggbildning, korrosion, partikelbildning, eller bäddagglomerering av sanden i fluidiserande bäddpannor. Dessa askrelaterade driftsproblem kan orsaka kostsamma underhållsåtgärder och i värsta fall driftstopp.

Med fokus på ökad användning av biomassa för bioenergi har denna avhandling undersökt effekten av lagring, bränsleledesign och processanpassning för att förbättra förbränningsegenskaperna hos restströmmar från skogs- och jordbruk. Detta genomfördes genom att först studera förändringar i barkegenskaper under lagring. Sedan genomfördes bränsleledesignåtgärder i form av mekanisk sållning och kalciumtillsatser på skogs- och jordbruksrester för att ändra bränslets kemiska sammansättning. Därtill studerades en processanpassningsåtgärd där olika sandbäddmaterials interaktioner med bränsleaskan utvärderades vid förbränning i en bubblande fluidbädd som ett alternativ till fall där bränsleledesignåtgärder inte är önskvärda/möjliga.

De övergripande resultaten visade på signifikanta förändringar i förekomst av vissa av barkens huvudbeståndsdelar i barkhögens yttre delar under lagring; dessa förändringar förväntas dock inte påverka egenskaperna vid förbränning. Den mekaniska sållningen minskade mängden aska i bränslet men medförde betydande biomassaförluster och förändrade inte askkemin

som önskat. Tillsats av kalcium ökade temperaturen för defluidisering genom att höja askans smälttemperatur, men tillsatsen innebär en förhöjd risk för bildning av korrosiva ämnen och ledde till höga koncentrationer av kolmonoxid i rökgaserna för både kvarts- och olivinbäddsmaterial som testades. Jämförelsen mellan tre bäddmaterial under förbränning i en bubblande fluidbädd visade hög interaktion mellan kvartspartiklar och bränsleaskan. Däremot visade olivin och fältspat låg interaktion med bränsleaskan. Trots detta visade sig fältspat som bäddmaterial vid förbränning av alkalirika bränslen såsom lignocellulosiska restströmmar från jordbruk vara den minst lämpliga av de testade bäddmaterialen. Alkali från fältspatspartiklar diffunderade ut och ökade därmed den totala mängden alkali i bädden vilket innebär en förhöjd risk för agglomerering. Sammantaget visar resultaten på alla åtgärder som tillämpas för att förbättra utnyttjandet av lignocellulosarester i bioenergitillämpningar bör överväga hur askkemin påverkas för att förbättra prestandan vid bränsleomvandling.

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This thesis evaluated the impact of storage, fuel design, and process adaptation for improving combustion characteristics of lignocellulosic residues. Changes were observed during bark storage but will not affect combustion characteristics. Screening did not change the ash chemistry and was associated with mass losses. Ca-addition increased defluidization temperatures but implied elevated risks for corrosion and extreme CO (g). The feldspar bed material reduced defluidization temperature. A good understanding of ash transformation reactions is needed to mitigate ash-related problems.

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