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Mitigation of Ash-related Problems by Additives during the Combustion of Solid Biomass

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Abstract

The formation of depositions on heat exchanger surfaces during the combustion of solid biomass drastically reduces the efficiency and lifetime of biomass-fired power plants. The growth of these slagging and fouling depositions on heat-exchanging surfaces is strongly linked to the presence of gaseous alkali species. The concentration of alkali species in the gas phase and, thus, the release of alkali species from biofuels are crucial factors in the deposition formation. A common measure to limit these ash-related problems is the reduction of process temperatures, which further decreases efficiency. Alternatively, additives can be employed to capture problematic alkali species and bind them in temperature-stable compounds. The understanding of the fuel-specific alkali release and the influence of additives is limited but necessary for the implementation of mitigation strategies. In this work, a method for the temperature-resolved analysis of the alkali release from biomass samples in an electrothermal vaporization (ETV) unit coupled to an inductively coupled plasma optical emission spectrometer (ICP-OES) is developed. This method is validated by comparison with four other analytical methods, including chemical fractionation (CF), X-ray fluorescence analysis (XRF), and microwave pressure digestion with two different solvents. The influence of the particle size on the release is evaluated and the temperature measurements are validated by analyzing pure substances with a distinct evaporation behavior. The elemental release from pure biofuels and the influence of kaolin and coal fly ash (CFA) on the potassium release are analyzed. The release patterns of the ETV measurements indicate that potassium is predominantly released as KOH or elemental potassium. The analysis of fuel and additive mixtures shows that the common fuel indices are not suitable for evaluating potassium release due to conflicting predictions regarding the use of additives and inconsistent ranking of the investigated fuels. Additives can shift the potassium release by up to 300 °C and can increase the ash stability. However, this positive effect is highly fuel-specific and could not be observed for mixtures of kaolin or CFA with beech wood. The transfer of the experimental results to the most common commercial combustion systems shows hardly any potassium release at the temperatures in fluidized bed systems. The peak temperatures in suspension combustion systems are so high that almost all potassium is released to the gas phase, even if additives are mixed with the fuel. Most of the potassium release occurs in the temperature range of grate combustion systems. In this temperature range, additives can significantly reduce the share of potassium that enters the gas phase. Moreover, reducing the temperature on the grate by changing the operating conditions could also drastically reduce the potassium concentration in the gas phase.

Overall, the ETV-ICP-OES results allow the comparison of different biofuels, highlight the relevant temperature range of alkali release, and narrow down the sensible field of application of additives during the combustion of solid biomass.

Kurzfassung

Die Bildung von Ablagerungen auf Wärmeübertragern bei der Verbrennung fester Biomasse führt zu einer drastischen Verringerung des Wirkungsgrads und der Lebensdauer von Biomassekraftwerken. Die Konzentration von Alkaliverbindungen in der Gasphase und damit die Freisetzung aus Biobrennstoffen sind entscheidende Faktoren für die Bildung von Ablagerungen. Eine gängige Maßnahme zur Begrenzung aschebedingter Probleme ist die Senkung der Prozesstemperaturen, wodurch die Effizienz weiter sinkt. Alternativ können Additive eingesetzt werden, um problematische Alkaliverbindungen in temperaturstabilen Verbindungen zu binden. Das Verständnis der brennstoffspezifischen Alkalifreisetzung und des Einflusses von Additiven ist begrenzt, aber für die Umsetzung von Minderungsstrategien entscheidend.

In dieser Arbeit wird eine Methode zur temperaturaufgelösten Analyse der Alkalifreisetzung aus Biomasseproben in einer elektrothermischen Verdampfungseinheit (ETV), die mit einem optischen Emissionsspektrometer mit induktiv gekoppeltem Plasma (ICP-OES) verbunden ist, entwickelt. Diese Methode wird durch den Vergleich mit vier anderen Analysemethoden validiert, darunter chemische Fraktionierung, Röntgenfluoreszenzanalyse und Mikrowellen-Druckaufschluss mit zwei verschiedenen Lösungsmitteln. Der Einfluss der Partikelgröße auf die Freisetzung wird bewertet und die Temperaturmessungen werden durch die Analyse von Reinsubstanzen mit unimodalem Verdampfungsverhalten validiert. Die Elementfreisetzung aus reinen Biobrennstoffen und der Einfluss von Kaolin und Kohleflugasche auf die Kaliumfreisetzung werden analysiert.

Die Freisetzungsmuster der ETV-Messungen zeigen, dass Kalium überwiegend als KOH oder elementares Kalium freigesetzt wird. Die Analyse der Brennstoff- und Additivmischungen verdeutlicht, dass die üblichen Brennstoffindizes für die Bewertung der Kaliumfreisetzung aufgrund widersprüchlicher Prognosen hinsichtlich des Additiveinsatzes und einer inkonsistenten Bewertung der untersuchten Brennstoffe nicht geeignet sind. Additive können die Kaliumfreisetzung um bis zu 300 °C verschieben und die Aschestabilität erhöhen. Dieser positive Effekt ist jedoch sehr brennstoffspezifisch und konnte bei Mischungen von Kaolin oder Kohleflugasche mit Buchenholz nicht beobachtet werden.

Die Übertragung der experimentellen Ergebnisse auf die gängigsten kommerziellen Verbrennungssysteme zeigt, dass bei den Temperaturen in Wirbelschichtsystemen kaum Kalium freigesetzt wird. Die Spitzentemperaturen in Staubfeuerungen sind so hoch, dass fast das gesamte Kalium in die Gasphase freigesetzt wird, selbst wenn dem Brennstoff Additive beigemischt werden. Der größte Teil der Kaliumfreisetzung findet im Temperaturbereich von Rostfeuerungen statt. In diesem Temperaturbereich können Additive den Anteil des freigesetzten Kaliums erheblich reduzieren. Darüber hinaus könnte eine Senkung der Temperatur am Rost durch Änderung der Betriebsbedingungen die Kaliumkonzentration in der Gasphase ebenfalls drastisch reduzieren.

Insgesamt ermöglichen die ETV-ICP-OES Ergebnisse den Vergleich verschiedener Biobrennstoffe, zeigen den relevanten Temperaturbereich der Alkalifreisetzung auf und grenzen den sinnvollen Einsatzbereich von Additiven bei der Verbrennung fester Biomasse ein.

Contents

1

Introduction

Public awareness of the impacts of climate change has increased due to more frequent extreme weather events and record-breaking temperatures. At the current rate of global warming, the Paris Agreement's goal of limiting anthropogenic climate change to well below 2 °C is becoming increasingly unrealistic and extremely ambitious. The prevailing trend that each new Intergovernmental Panel on Climate Change (IPCC) report presents an even more drastic picture of climate change, both in the measured data and the resulting projections, highlights the need for rapid action. [1, 2]

The use of biomass can play a decisive role in the transition to a sustainable energy system. Biomass can be stored well and can compensate for seasonal and shorter-term volatility of other renewable energies. In Germany, the combustion of solid biomass generated over 11 TWh_{el} of electricity in 2022, which corresponds to approx. 2 % of the total electricity demand. With over 130 TWh_{th}, the combustion of solid biomass was responsible for about two-thirds (65 %) of the heat supply from renewable energies in Germany in the same period. The biogenic part of municipal solid waste (MSW) is not included in these numbers [3].
Worldwide, biomass supplies more than half of the renewable energy, with solid biomass accounting for the vast majority [4]. Global biomass use is below sustainable capacity, so there is potential to increase biomass use. However, some regions, such as Asia, are using more than the sustainable amount [5]. The most relevant pathway to increase the energy output of biomass is increased conversion efficiency. There are a variety of biomass combustion methods ranging from simple open fires to sophisticated combustion systems. Therefore, increasing conversion efficiency can involve a wide range of measures. In addition to increased energy efficiencies, improved combustion systems could contribute to achieving several sustainable development goals defined by the United Nations [6].

The need to increase the efficiency and improve the technology of advanced combustion systems is driven by multiple factors. Fuel efficiency is an important aspect of the economic performance of combustion systems and technical innovation can be a competitive advantage [7]. Moreover, material use will play an increasingly important role in the utilization of biomass [8]. This will likely reduce the availability of high-quality biofuels such as wood for combustion. Therefore, more challenging biofuels such as agricultural residues, waste wood, and energy crops will become even

more relevant.
However, certain ash-related problems arise during the combustion of solid biomass that are linked to the fuel quality. The release of alkali compounds causes fine particle emissions and results in deposition formation on parts of the combustion system. In small-scale combustion systems, the emission of fine particles is regulated, and increased fine particle emissions make post-treatment of flue gases necessary. In commercial combustion systems, deposition formation on heat-exchanging surfaces is a major challenge. These depositions significantly reduce the efficiency, and also cause corrosion that drastically shortens the life of the affected components. [9–11]
Additives can be used to mitigate these problems of fine particle and deposition formation. Aluminosilicate-based additives like kaolin or coal fly ash (CFA) can capture alkali species and bind them in temperature-stable compounds. Thus, the concentration of problematic species in the gas phase and the associated problems can be reduced significantly [12].
Temperature-resolved data on alkali release is critical for the efficient management of fine particle emissions and depositions during solid biomass combustion. However, the release behavior is fuel-specific and the existing literature data is insufficient.

The goal of this thesis is to evaluate ash-related problems of diverse biofuels in different combustion systems and the effect of additives based on experimental results. First, a method for the analysis of biomass samples in an electrothermal vaporization (ETV) unit coupled with an inductively coupled plasma optical emission spectrometer (ICP-OES) is developed. The temperature-resolved release of side elements from a wide range of biomass samples is investigated. Additionally, the influence of additives on the potassium release behavior is analyzed. Finally, the experimental results are applied to the most relevant biomass combustion systems.

1.1 Structure of this Thesis

This publication-based dissertation begins with a review of previous work in the field of biomass combustion at the chair of energy systems and an overview of the publications of this work. After the introduction, the fundamentals of biomass combustion and the elemental release from biomass are outlined. Additionally, the ash-related problems in power plants and the inclusion of problematic species in additives are described in detail. After the literature review, the research question of this work is outlined. Next, the experimental setup of the ETV-ICP-OES system is explained in detail, as it forms the basis for all publications in this thesis. All papers are summarized and the contribution of each author is outlined. An overarching summary is provided at the end of the thesis, along with a critical discussion and a brief outlook on future research in this area. Finally, the appendix lists the articles as they appear in the journals.

1.2 Previous Work at the Chair of Energy Systems

Over the past two decades, the chair of energy systems has extensively researched alkali-related problems and their mitigation by additives. The research has covered not only combustion but also integrated gasification combined cycle (IGCC) processes. Over the years, the research focus has shifted from coal to biomass. This work builds on the research experience of the chair of energy systems. The most important previous works in the field of biomass combustion are presented below.

Kleinhans provided a detailed description and analysis of ash-related problems in coal and biomass combustion and the underlying mechanisms based on experimental results and computational fluid dynamics (CFD) simulations. The comprehensive literature review allows the identification of common fuel characteristics and important differences between coal and biomass [11, 13].
Balan investigated the influence of the fuel composition on the combustion behavior and the deposition formation in a pilot-scale entrained flow reactor [10]. The influence of co-firing straw and coal on the flue gas composition and deposition formation was investigated by Wolf [14]. Stephan analyzed the influence of additives on particle formation and the corrosion potential on a laboratory scale and in an industrial-scale biomass power plant [15].
The most important previous research for this work was carried out by Kerscher, who experimentally analyzed both the alkali release from fuels and the inclusion of alkali species in additives. He used several analytical methods to investigate the alkali release from hard coal, lignite, and torrefied wood. The effect of various experimental influencing factors was analyzed in a wire mesh reactor, an entrained flow reactor, a tube furnace, and by thermogravimetric analysis (TGA). Moreover, a molecular beam mass spectrometer (MBMS) connected to an electrically heated furnace allowed the online analysis of the alkali release. Kerscher implemented the results in a single first-order reaction model to describe the alkali release during devolatilization. Besides the alkali release, he investigated the alkali sorption in kaolin, bentonite, and bauxite and described the sorption process with a mass-specific sorbent loading combined with an n-th order rate equation [12, 16, 17].
Nowak Delgado investigated the effect of additives on ash-related problems in a pilot-scale biomass pulverized fuel combustion system. His work focused on the influence of additives on the formation of fine particle emissions and the impact of the additive surface area. For the addition of coal fly ash during the pulverized wood combustion he showed a reduction in the fine particle emissions and a shift of the potassium concentration from smaller to larger particles. These experiments are a valuable reference since the fuels and additives studied by Nowak Delgado are also analyzed in this thesis [18, 19].
The numerical description of the release of alkali species and the inclusion in additives was carried out by de Riese. He combined experimental data and thermodynamic equilibrium calculations in CFD simulations of pulverized fuel combustion systems. His simulations emphasize the inclusion of KOH in aluminum-silicate-based additives by showing that the capture of KCl and K_2SO_4 can be modeled by the capture of KOH and gas phase reactions. He also used thermodynamic equilibrium calculations to show the strong influence of the chemical composition of the additive on the maximum alkali capture and thermal stability. Since alkali compounds in ash follow similar reaction pathways, these results highlight the need for temperature-resolved alkali release analysis [20–22].

1.3 Publications

In this section, the publications of this dissertation are listed. Four of the five papers have been published in peer-reviewed journals. Paper II was published at the "Deutscher Flammentag" conference. A summary of each paper and the contribution of each author is given in a corresponding chapter. Figure 1.1 summarizes the publications of this dissertation. The papers evolve from a general evaluation of the analytical method of electrothermal vaporization to an application of the laboratory results to combustion systems.

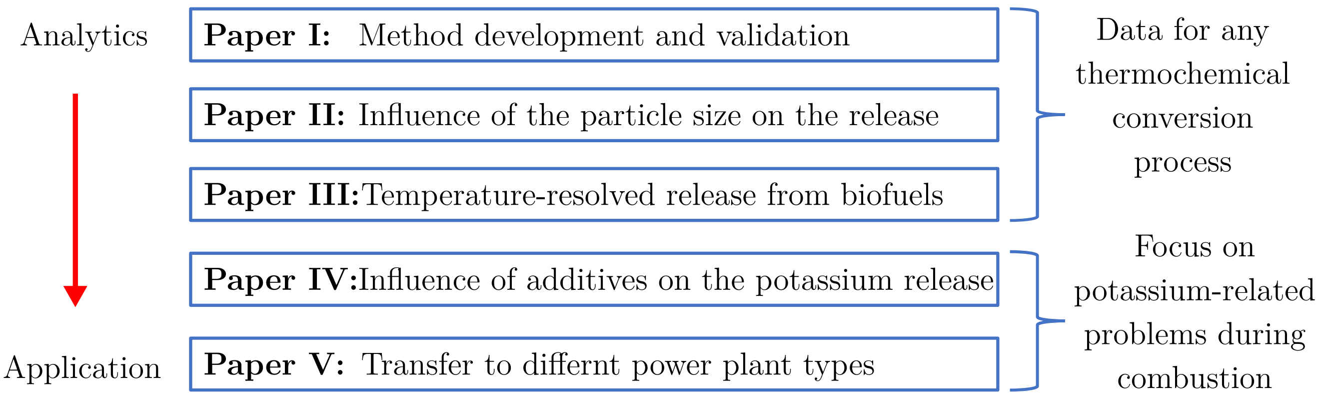


Figure 1.1: Overview of the main publications of this dissertation.

- **Paper I.:** H. Mörtenkötter, D. Grünwald, S. Fendt, and H. Spliethoff: "Validation of Electrothermal Vaporization for the Analysis of Biomass Samples and Comparison with other Methods of Analysis", *Waste and Biomass Valorization*, Volume 14, pages 3489–3502, 2023, https://doi.org/10.1007/s12649-023-02129-0 [23]
- **Paper II.:** H. Mörtenkötter, C. Heilmeier, T. de Riese, S. Fendt, and H. Spliethoff, "Temperaturaufgelöste Freisetzung von Nebenelementen aus fester Biomasse", *31. Deutscher Flammentag*, 2023 [24]
- **Paper III.:** H. Mörtenkötter, C. Heilmeier, T. de Riese, S. Fendt, and H. Spliethoff: "Temperature resolved release of inorganic compounds from biomass", *Fuel*, Volume 357, 2024, https://doi.org/10.1016/j.fuel.2023.129939 [25]
- **Paper IV.:** H. Mörtenkötter, M. Kulkarni, L. Fuchs, F. Kerscher, S. Fendt, and H. Spliethoff, “Effects of aluminosilicate-based additives on potassium release and ash melting during biomass combustion”, *Fuel*, vol. 374, p. 132471, 2024, https://doi.org/10.1016/j.fuel.2024.132471 [26]
- **Paper V.:** H. Mörtenkötter, F. Kerscher, M. Schönsteiner, S. DeYoung, S. Fendt, and H. Spliethoff: “Potassium release and mitigation by additives in different biomass combustion systems,” *Fuel*, Volume 369, p. 131800, 2024, https://doi.org/10.1016/j.fuel.2024.131800 [27]

In addition to the core publications of this thesis, a number of other publications have been published during the time at the Chair of Energy Systems. These publications are listed below and include conference contributions, project reports, and co-authored papers.

- H. Mörtenkötter, S. Fendt, H. Spliethoff: "Temperature-resolved Experimental Investigation of the Alkali Release during the Combustion of Solid Biomass", *European Biomass Conference & Exhibition*, Oral presentation, 2021
- R. Nowak Delgado, H. Mörtenkötter, S. Fendt, H. Spliethoff: "Sampling of Fine Particles (PM2. 5) in a Pilot Scale Swirl Burner Test Rig Combusting Torrefied Wood with Coal Fly

Ash and Kaolin", *53. Kraftwerkstechnisches Kolloquium*, Poster presentation, 2021

- H. Mörtenkötter, V. Padovan, S. Fendt, H. Spliethoff: "Experimental Investigation of Mineral Sorbents for Alkali Removal during the Combustion of Solid Biomass" *13th European Conference on Industrial Furnaces and Boilers (INFUB-13)* , Conference paper and poster presentation, 2022
- H. Mörtenkötter, D. Grünwald, S. Fendt, and H. Spliethoff: "Influence of the Chemical Association Form of Alkali Compounds on the Release Behavior from Solid Biomass.", *9th International Conference on Engineering for Waste and Biomass Valorisation*, Oral presentation, 2022
- H. Mörtenkötter, S. Fendt, H. Spliethoff: "Alkali Removal by Mineral Sorbents in a Novel Two-staged Thermogravimetric Analysis System", *European Biomass Conference & Exhibition*, Oral presentation, 2023
- H. Mörtenkötter, S. Fendt, H. Spliethoff: "Schlussbericht zum Vorhaben: Feinstaub- und Depositionsreduktion durch Additive bei der Biomassefeuerung", 2024, https://www.fnr.de/index.php?id=11150&fkz=2219NR023
- H. Mörtenkötter, F. Kerscher, M. Schönsteiner, S. DeYoung, S. Fendt, and H. Spliethoff: "Release of inorganic compounds in biomass combustion systems" *10th International Conference on Engineering for Waste and Biomass Valorisation*, Oral presentation, 2024
- M.Ritz, M. Dossow, H. Mörtenkötter, S. Fendt, H. Spliethoff: "Experimental investigation of heavy metal release in entrained-flow gasification", *Fuel*, Volume 387, p. 134379, 2025, https://doi.org/10.1016/j.fuel.2025.134379 [28]

2

Fundamentals

This chapter gives a general overview of the combustion of solid biomass. First, the composition of biomass is discussed and different types of solid biofuels are categorized. The combustion of biomass is reviewed, with a special emphasis on the different types of commercial power plants for electricity generation. Afterward, the release of alkali species from solid biomass is described in detail. Literature data is analyzed, and different measurement methods for the alkali release are discussed. In addition, mechanisms and models for the alkali release are presented. Then, the problems associated with potassium release, fine particle and deposition formation are described. Finally, the inclusion of alkali species in additives is discussed.

2.1 Biomass Composition

In general, biomass can be defined as every substance that is or has been a part of a living organism. This includes living and dead plants and animals, their residues, and all further processed materials of such origin [9]. While fossil fuels also originate from dead plants and animals, they are not considered to be biomass. The youngest form of fossil fuel, peat, is on the borderline between biomass and fossil fuel in literature but is not considered biomass in this work since its formation is not sustainable in human timescales [29, 30]. Biomass-containing waste products are counted as biomass in some sources, but in this work, these waste products are considered waste fuels [31]. In the context of this work, biomass can be defined as organic fuels from forestry or agriculture.

Since this definition is very broad, a further division into categories is useful. Primary biomass is formed by the direct conversion of solar energy through photosynthesis, hence all plants are considered primary biomass. Primary biomass can be further categorized, based on the origin, into energy crops, woody biomass, stalk-like biomass, and algae. Secondary biomass is the result of the digestion or conversion of primary biomass in living organisms e.g. animal waste. The products of technical conversion of primary and secondary biomass, such as liquid biofuels, torrefied wood, or paper, are tertiary biomass. [9]

Biomass consists of elongated cells connected by pits [32]. On a cellular level, biomass is usually divided into cell wall components, extractives from the lumina of the living cell, and ash [33]. In the following, the molecular structure is briefly explained, and then the elemental composition of biomass is discussed.

Molecular Structure of Biomass

The conversion of solar energy through photosynthesis is the driving force for biomass growth. In this process, light energy is converted into chemical energy. In the dominating form of photosynthesis, carbon dioxide (CO_2) and water (H_2O) are synthesized into carbohydrates. Equation 2.1 shows the chemical equation of a photosynthesis route to glucose ($C_6H_{12}O_6$). [34]

$$6 \cdot \mathrm{CO_2} + 6 \cdot \mathrm{H_2O} + \mathrm{Energy/\,Light} \longrightarrow \mathrm{C_6H_{12}O_6} + 6 \cdot \mathrm{O_2} \qquad \Delta\mathrm{H} = +2870\,\frac{\mathrm{kJ}}{\mathrm{mol}} \tag{2.1}$$

In polymerisation processes the monomers resulting from the photosynthesis add up to extractives and cell wall components. The cell wall compounds cellulose, hemicellulose and lignin are the main constituents of biomass. In wood, these three polymers account for 95 % of the dry weight [9].

Cellulose $(C_6H_{10}O_5)_n$ is the main component of cell walls. It is an unbranched polymer of hundreds to ten thousand glucose monomers. Cellulose is responsible for the tensile strength of biomass and the polysaccharide is the most common organic substance in nature [9, 34].

Hemicelluloses is a broad term used for heterogeneous polysaccharides [32]. Hemicellulose molecules are branched and interconnect cellulose in the cell wall [33]. This important interconnection contributes to the strength of the cell wall. Although the term is technically outdated to describe these molecules, it is still commonly used to describe cell wall polysaccharides different from cellulose and pectin [35].

Lignins are polymers consisting mainly of aromatic phenyl propane units [36]. The amorphous and highly complex lignins surround cellulose fibers and give the cell walls strength through this encrustation [33]. The highest lignin fraction is found in wood and accounts for up to 40 % of the dry weight. The term lignin originates from the Latin word for wood, lignum [34]. There is no commercial system for splitting lignin into its aromatic constituents because it is very difficult to break down biochemically. Furthermore, there are few applications for the direct use of lignin. Even in processes in which other components of biomass are utilized, such as paper production, lignin is usually used thermally [9].

The term extractives refers to a wide range of low molecular weight components that are soluble in water or neutral organic solvents. These extracellular organic compounds have no covalent bonds with the cell wall and are present in the porous structure of the biomass. Extractives can be lipophilic or hydrophilic [32, 37].

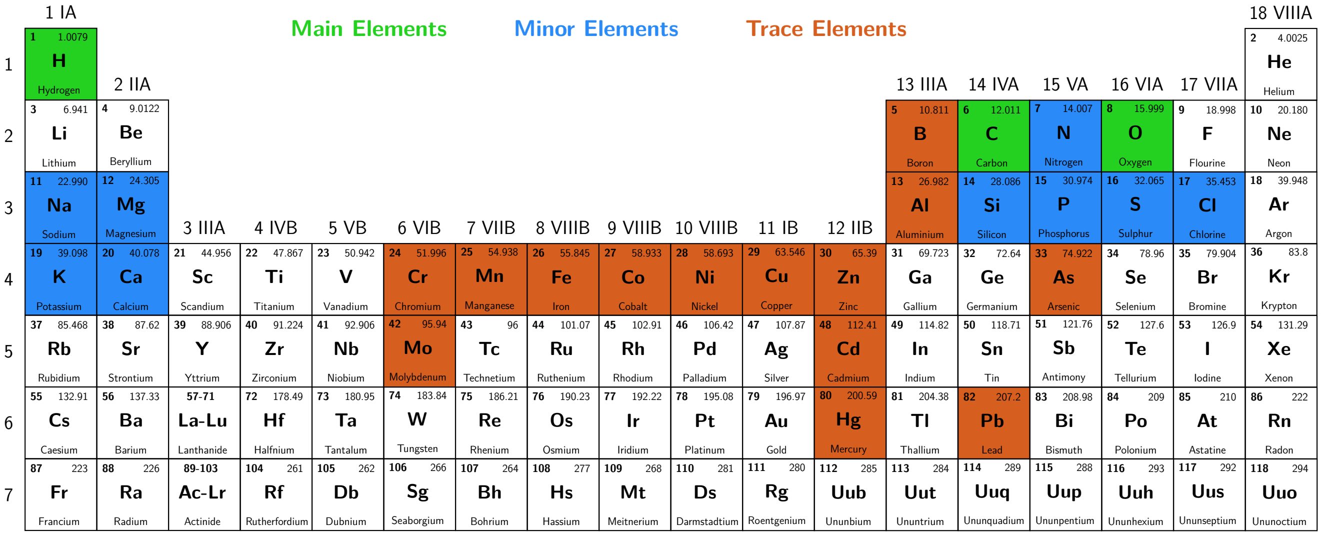
All inorganic compounds of biomass are summarised as ash. Ash compounds are present in the cell wall, the extractives, and the lumina of the cell, mostly in the form of salt deposits [32]. Parts of the ash are soluble in extraction processes, whereby the soluble inorganics are counted as ash and not as extractives. Hence, the ash content of the biomass can be further differentiated into soluble inorganic salts and structural ash, i.e. the inorganics remaining in the biomass after an extraction process [30].

Elemental Composition of Biomass

The elemental composition of biomass is of great interest for many processes in the life cycle of biomass, such as growth, pollutant formation during combustion, ash utilization, or recycling of phosphorous. Depending on biomass type, location, the use of fertilizers, the harvesting method, and potential after-treatment, the elemental composition of biomass and the utilization behavior vary drastically [31]. In this subsection, a general overview of the elements present in biomass is given, focusing on the ash and deposition-forming substances.

The elements present in biomass can be categorized into main-, minor-, and trace elements. A uniform categorization based on the concentration or function of the respective element can be difficult, as these factors are variable for different biomass types and locations. In literature, the definitions usually vary, depending on whether the work focuses on plants or on thermal conversion processes [9, 38, 39]. In this work, main-, minor-, and trace elements are categorized as follows: the main elements carbon (C), hydrogen (H), and oxygen (O) make up the products of photosynthesis. The macronutrients nitrogen (N), sulphur (S), phosphorous (P), magnesium (Mg), calcium (Ca) and potassium (K) are minor elements. The beneficial elements sodium (Na) and silicon (Si), as well as the micronutrient chlorine (Cl), are also considered minor elements since their concentration in biomass regularly exceeds 100 $\frac{mg}{kg}$ or $0,01\ wt\%$ [38]. All other elements present in biomass are considered trace elements. Table 2.1 shows a periodic table of elements in which the elements contained in biomass are highlighted.

Table 2.1: Periodic table of the elements highlighting the major, minor and trace elements in biomass. Adapted from [9, 40, 41]. Published in paper II [25].



🟩 Main Elements   🟦 Minor Elements   🟧 Trace Elements

	1 IA	2 IIA	3 IIIA	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	🟩 1 1.0079 **H** Hydrogen																	2 4.0025 **He** Helium
2	3 6.941 **Li** Lithium	4 9.0122 **Be** Beryllium											🟧 5 10.811 **B** Boron	🟩 6 12.011 **C** Carbon	🟦 7 14.007 **N** Nitrogen	🟩 8 15.999 **O** Oxygen	9 18.998 **F** Flourine	10 20.180 **Ne** Neon
3	🟦 11 22.990 **Na** Sodium	🟦 12 24.305 **Mg** Magnesium											🟧 13 26.982 **Al** Aluminium	🟦 14 28.086 **Si** Silicon	🟦 15 30.974 **P** Phosphorus	🟦 16 32.065 **S** Sulphur	🟦 17 35.453 **Cl** Chlorine	18 39.948 **Ar** Argon
4	🟦 19 39.098 **K** Potassium	🟦 20 40.078 **Ca** Calcium	21 44.956 **Sc** Scandium	22 47.867 **Ti** Titanium	23 50.942 **V** Vanadium	🟧 24 51.996 **Cr** Chromium	🟧 25 54.938 **Mn** Manganese	🟧 26 55.845 **Fe** Iron	🟧 27 58.933 **Co** Cobalt	🟧 28 58.693 **Ni** Nickel	🟧 29 63.546 **Cu** Copper	🟧 30 65.39 **Zn** Zinc	31 69.723 **Ga** Gallium	32 72.64 **Ge** Germanium	🟧 33 74.922 **As** Arsenic	34 78.96 **Se** Selenium	35 79.904 **Br** Bromine	36 83.8 **Kr** Krypton
5	37 85.468 **Rb** Rubidium	38 87.62 **Sr** Strontium	39 88.906 **Y** Yttrium	40 91.224 **Zr** Zirconium	41 92.906 **Nb** Niobium	🟧 42 95.94 **Mo** Molybdenum	43 96 **Tc** Technetium	44 101.07 **Ru** Ruthenium	45 102.91 **Rh** Rhodium	46 106.42 **Pd** Palladium	47 107.87 **Ag** Silver	🟧 48 112.41 **Cd** Cadmium	49 114.82 **In** Indium	50 118.71 **Sn** Tin	51 121.76 **Sb** Antimony	52 127.6 **Te** Tellurium	53 126.9 **I** Iodine	54 131.29 **Xe** Xenon
6	55 132.91 **Cs** Caesium	56 137.33 **Ba** Barium	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** Halfnium	73 180.95 **Ta** Tantalum	74 183.84 **W** Tungsten	75 186.21 **Re** Rhenium	76 190.23 **Os** Osmium	77 192.22 **Ir** Iridium	78 195.08 **Pt** Platinum	79 196.97 **Au** Gold	🟧 80 200.59 **Hg** Mercury	81 204.38 **Tl** Thallium	🟧 82 207.2 **Pb** Lead	83 208.98 **Bi** Bismuth	84 209 **Po** Polonium	85 210 **At** Astatine	86 222 **Rn** Radon
7	87 223 **Fr** Francium	88 226 **Ra** Radium	89-103 **Ac-Lr** Actinide	104 261 **Rf** Rutherfordium	105 262 **Db** Dubnium	106 266 **Sg** Seaborgium	107 264 **Bh** Bohrium	108 277 **Hs** Hassium	109 268 **Mt** Meitnerium	110 281 **Ds** Darmstadtium	111 280 **Rg** Roentgenium	112 285 **Uub** Ununbium	113 284 **Uut** Ununtrium	114 289 **Uuq** Ununquadium	115 288 **Uup** Ununpentium	116 293 **Uuh** Ununhexium	117 292 **Uus** Ununseptium	118 294 **Uuo** Ununoctium

Main Elements

The main elements make up more than 90% of the weight of biomass. Their concentration influences the energy content considerably, as the idealistic calculation of the lower heating value (LHV) in equation 2.2 shows. The share of the respective element is inserted in decimal notation. The calculated heating value usually deviates in the range of less than five percent from measured values. [9]

$$\mathrm{LHV_{wf}} = 34{,}8\,\mathrm{C} + 93{,}9\,\mathrm{H} + 10{,}5\,\mathrm{S} + 6{,}3\,\mathrm{N} - 10{,}8\,\mathrm{O} \qquad [\frac{\mathrm{MJ}}{\mathrm{kg}}] \tag{2.2}$$

Carbon The most important element in biomass is carbon. As described in section 2.1, carbon is a key element in photosynthesis. Compared to coal, the carbon fraction in biomass is significantly lower [31]. In the case of incomplete combustion, carbon compounds can lead to harmful emissions such as carbon monoxide (CO) and soot. The particulate matter (PM) emissions of organic soot are a result of poor mixing and low temperatures and occur especially in small-scale wood-burning units. PM emissions due to organic soot differ from inorganic PM emissions because organic soot emissions can be overcome by more advanced combustion systems [9, 42, 43].

Hydrogen Hydrogen is an integral part of the molecules resulting from photosynthesis. Additionally, by creating proton gradients, it plays a central role in regulating the electron transport necessary for photosynthesis and respiration [44]. The oxidation of carbon and hydrogen are the exothermic reactions that release the most energy and drive the combustion [9, 45].

Oxygen The oxygen content in biomass is significantly higher than in coal [31]. The oxygen bound in the biomass supports the combustion but reduces the calorific value because compounds are already oxidized to a certain degree [9, 45].

Minor Elements

As described above, there is no uniform definition of minor elements in literature, so in this work, the elements that regularly exceed concentrations of 100 $\frac{mg}{kg}$ or $0,01\ wt\%$ are considered minor elements. The minor elements in biomass are primarily macronutrients, essential for the growth and survival of the plant [44]. According to the "Law of the Minimum" published by Justus von Liebig in 1841, the growth of plants is limited by the scarest resource and not by the total available resources [46, 47]. Hence, the lack of just one essential nutrient in the soil can diminish the plant's growth and yield. Fertilizers are used to overcome this problem. Thus, the concentrations of minor elements are intentionally altered. Additionally, the location and the harvesting procedure influence the minor element concentration in biomass. Of all influencing factors, however, the plant species is the most important one. [9, 48]

A basic understanding of the minor elements is necessary for the development of an analytical method to evaluate matrix effects and possible interferences. In addition, minor elements are relevant to deposition formation and corrosion problems. Minor elements determine ash composition and ash behavior. Therefore, the concentration of minor elements is crucial for the optimization of biomass utilization. In the following, the minor elements in biomass are listed according to their molar weight.

Nitrogen As a building block of amino acids, enzymes, proteins, and nucleic acids, nitrogen is pivotal in any organism [38]. In plants, nitrogen additionally influences photosynthesis by increasing the formation of relevant compounds [49]. Nitrogen concentration varies between different biomass types and cultivation methods. The nitrogen concentration of wood is significantly lower than that of coal, but stalk-like biomass such as straw can have equally high or higher nitrogen concentrations [31]. Due to its relevance, nitrogen is often supplemented by fertilization. Fertilization can have significant local and global environmental impacts. Nitrates contained in fertilizers can enter groundwater. Both the energy-intensive production process and the application of fertilizers can lead to greenhouse gas emissions and must be taken into account when assessing the sustainability of biomass [50]. During combustion, the nitrogen contained in biomass is partially oxidized to nitrogen oxides (NOx) and thus leads to harmful emissions [9, 50].

Sodium Sodium can be adsorbed in relatively high amounts as a cation from the soil. It is important for the establishment of the osmotic potential in the plant [38]. During combustion, sodium can form fine particle emissions and influences the ash melting behavior [9].

Magnesium Magnesium plays an important role in plant enzyme regulation and in regulating the cellular pH-value [38]. It is an ash-forming element and can contribute to the absorption of pollutants into the ash [9].

Silicon Silicon is taken up from the soil [38]. Its nutritional influence is not entirely clear and plant-specific. Silicon is one of the most important ash-forming elements in terms of quantity. [9, 45]

Phosphorus As a component of nucleic acids, phosphorous is a pivotal component of DNA and RNA. Since phosphorus is unsubstitutable in these functions, it is a necessity of life [51]. Especially in food production, phosphorus fertilizer, obtained from rock phosphate, is necessary for high crop yields. The reserves of the non-renewable rock phosphate are predicted to be depleted within the next 50-100 years [38]. The challenge of high-yield food production for a growing world population and exhaustible fertilizer reserves make phosphate recycling necessary. Therefore, ash utilization with a focus on phosphorus recycling is likely to play an important role in biomass combustion. This is already the case for sewage sludge combustion. [9, 52]

Sulphur As a structural component of proteins, amino acids, and coenzymes, sulphur is an essential nutrient. It is taken up both as SO_2 from the air and as sulphates through the roots. However, soil uptake is the most important mechanism [38]. During combustion large parts of the sulphur are released into the gas phase and form sulphur oxides (SOx) and alkali sulphates (Na_2SO_4, K_2SO_4). Sulphur emissions are highly problematic since SOx-emissions have significant impact on human health. The alkali sulphates condense when the flue gas cools down and cause harmful fine particle emissions. [9, 53].

Chlorine Chlorine is needed in plants for the establishment of electric and osmotic potentials [38]. The chlorine concentration differs between different biomass types. In stalk-like biomass, the chlorine concentration can be significantly higher than in coal. Chlorine is taken up by the roots, so the chlorine concentration in the plant increases with the chlorine concentration in the soil. This is the case in fertilized cultures because chlorine is an accompanying element in many fertilizers, and also in coastal areas, due to the increased concentration of salt (NaCl) in maritime air [31, 54]. During combustion, chlorine forms volatile compounds like HCl, Cl_2, and alkali chlorides $(NaCl, KCl)$. Thus, chlorine causes pollutant emissions as well as operational problems since the alkali chlorides can condense in the boiler section and lead to severe corrosion problems [9, 53].

Potassium Potassium is an essential nutrient due to its role in the plant-water relations and in establishing electro-potentials. Additionally, potassium is required for the synthesis of proteins [38]. Potassium is the predominant alkali metal in most biomass types and is frequently supplemented by fertilizers [53]. The potassium concentration varies considerably between different biomass types and is elevated in stalk-like biomass such as straw and miscanthus. During combustion, potassium causes fine particle emissions and deposition build-up on power plant surfaces. The potassium-containing depositions additionally cause severe high-temperature corrosion. [9, 10, 53]

Calcium Calcium is an essential macronutrient needed for the establishment of the osmotic potential and electro-potentials in plants. As calcium pectate, it can also be a structural cell wall component [44]. The calcium concentration varies considerably, not only among different types of biomass, but also within different parts of the same plant. It is elevated in roots and bark and can reach more than 10 % of the dry weight in mature leaves [38]. In thermal conversion processes, calcium can bind problematic species in the ash [9, 31].

The broad composition of different biomass types is shown in table 2.2. Two coals are listed as a reference. While the concentration of the main elements is relatively similar between the different biomass types, the moisture and the ash content vary drastically between the different biomass types and even between different samples of the same plant type.

Table 2.2: Ultimate analysis, calorific value, moisture, and ash content of different biofuels. Values are averages of multiple analyses of the respective fuels listed in the Phyllis 2 database [55]. Hard coal and lignite are listed as a reference [31]

Fuel	**C**	**H**	**O**	**N**	**S**	**LHV**	**Moisture**	**Ash**
		wt.% (DAF)				**MJ/kg**	**wt. %**	**wt. %**
Conventional woody fuels								
Beech wood [55]	47.37	6.20	46.19	0.20	0.06	18.1 - 18.6	5.9 - 19.0	0.6 - 1
Wood pellets [55]	49.59	6.33	44.71	0.20	0.02	17.9 - 19.4	5.2 - 14.7	0.3 - 2.4
Alternative woody fuels								
Spruce bark [55]	52.85	5.99	40.87	0.43	0.05	17.8 - 21.0	0.5 - 8.7	2.3 - 5.4
Torrefied wood [55]	53.61	5.86	40.80	0.18	0.02	19.6 - 21.2	0 - 5.6	2.6 - 5.4
Forest residue spruce [55]	52.57	6.11	40.61	0.67	0.03	19.6 - 20.1	6.3	1.3 - 4.1
Stalk-like biofuels								
Miscanthus [55]	49.63	5.63	43.81	0.54	0.06	15.6 - 21.0	7.3 - 49.0	1.5 - 7.5
Wheat straw [55]	49.03	5.96	43.95	0.69	0.14	15.2 - 20.5	0 - 17.4	4.7 - 12.3
Coal as reference								
Ruhr basin soft fat coal [31]	90.70	4.10	2.10	1.70	0.50	28.5 - 29.3	7.0 - 10.0	6.0 - 9
Rhineland soft brown coal [31]	68.30	5.00	27.50	0.50	1.40	6.3 - 9.6	50 - 62	6.3 - 9.6

Trace Elements

Plants can absorb around 60 different elements from the soil, so biomass can contain various trace elements. Many trace elements are unnecessary for the growth of the plant [44]. The concentration of trace elements usually does not exceed 100 $\frac{mg}{kg}$ or $0,01$ % of the dry weight. However, the concentration is highly dependent on the type of plant and soil, so it can be significantly higher. Most trace elements found in biomass are heavy metals. The ability of some plants to take up and concentrate certain harmful elements from the soil can be employed for phytoremediation. In this process, selected plants are planted on contaminated soil to reduce the concentration of harmful substances in the ground. This enables the energetic use of contaminated land that can not be used for food production while also rehabilitating the soil [56]. Due to their low concentration and temperature stability, trace elements play a minor role in combustion. After combustion, most trace elements are found in the fly ash or bottom ash. For ash utilization and recycling, the concentration of certain trace elements is of great interest [53, 57].

In general, biofuels are composed of a variety of elements in a broad range of concentrations. Notably, the concentration of ash-forming elements can vary significantly between different types of biomass, different parts of the same plant, and different growing locations.

2.2 Combustion of Solid Biomass

The combustion of biomass aims to release the chemically bound energy of the fuel. This release takes place in a heterogeneous oxidation process that converts the chemically bound energy into sensible heat. Heterogeneous oxidation processes are characterized by multiple phase changes and are, therefore, more complex than the combustion of gaseous fuels. The combustion process can be categorized into the steps of heating and drying, devolatilization, combustion of volatiles, and char burnout. [31, 42, 58]

In the initial heating step, water is released from the biomass. The drying process starts at around 100 °C and continuous to over 200 °C [31]. Since the combustion supplies the enthalpy of evaporation, the moisture content of the biomass significantly influences the net heat output.

If the biomass is heated further, volatile matter is released. The devolatilization of biomass starts in a temperature range between 160 °C and 250 °C, which is significantly lower compared to coal [42].

During devolatilization, macro molecules like cellulose and lignin are thermally exited to the degree that some of the inner molecular bounds dissociate [9]. Since biomass consists to a large part of these long-chained hydrocarbons, the volatile content is around 75% higher than that of coal [31, 59]. The volatile matter released from the biomass mainly consists of light hydrocarbons. The most prominent light gases released are CO, CO_2, H_2O, CH_4, CH_3OH, and CH_2O_2. Additionally, a variety of partly oxidized longer hydrocarbons is released into the gas phase. The volatile components are crucial for the ignition and stability of the flame. [59, 60]

Inorganic compounds influence the devolatilization behavior. The devolatilization process can differ significantly between different types of biomass. Hence, the release behavior of natural biomass can not be calculated by the macromolecular structure or the ratio of the main elements [60]. On top of influencing the organic release, some inorganic compounds are released during the devolatilization step.

The solid residue of the devolatilization is char. It consists of inorganic ash and fixed carbon since most hydrogen is released during the devolatilization [60].

In the gas phase, the volatile compounds react with oxygen and are combusted. Due to the variety of volatile species, the reaction chemistry is multifaceted. The oxidation of long-chain hydrocarbons is particularly complex because multiple intermediate species can be formed following a variety of reaction pathways [58]. In general, the volatile hydrocarbons react with oxygen to carbon dioxide (CO_2) and water (H_2O). This combustion process releases most of the chemically bound energy and drives the heating, drying, and devolatilization of the fuel [61]. The combustion of volatiles is rapid and usually limited by the rate of the volatile release [62].

In the last step of the combustion, char is oxidized. The solid residue of devolatilization consists mainly of fixed carbon. The carbon is oxidized in a heterogeneous surface reaction. In this process, H_2O or CO_2 molecules attach to the char surface and are reduced by the solid C to H_2 or CO. The products then detach from the surface. Afterward, CO is oxidized to CO_2 in a homogeneous gas phase oxidation predominantly via OH radicals [61]. The mechanism involves the adsorption of molecules at the surface, surface reactions, desorption of the products, pore diffusion, and gas phase diffusion. The overall reaction rate is limited by the slowest step. Since the mechanisms are highly temperature-dependent, different steps are rate-limiting at different temperatures. At low temperatures, the surface reaction is rate limiting, while at higher temperatures, the pore diffusion or the gas phase diffusion becomes the limiting process. [58]

Combustion Systems

The combustion behavior of biomass strongly depends on fuel type, particle size, moisture content, and the firing system. In this subsection, five different firing systems are compared. First, manual operated batch systems are analyzed. Then, pellet systems for residential applications are briefly explained. Afterward, the three most common firing systems for power generation, grate firing, fluidized bed, and suspension firing, are discussed.

Residential combustion systems can be categorized into manually operated batch systems and automatized pellet systems. Manually operated batch systems are long-established firing systems and are widely spread in household applications. Due to the high fine particle emissions that arise in residential areas, these systems are problematic. Manually operated residential biomass combustion systems were responsible for 17,4 % of all $PM_{2,5}$ emissions in Germany in 2015 [63]. The fine particle emissions of manually operated batch systems originate from inorganic species and avoidable, incomplete combustion. Fuel type, combustion cycle, and operating conditions drastically influence the overall fine particle emissions. In poor operating conditions or during certain combustion periods, organic soot can be responsible for over 90 % of the fine particle emissions [63, 64]

Periodic use, untrained operators, varying fuel quality, cyclic batch burning, and especially high organic soot emissions are challenges for an additive-based fine particle reduction system. Most likely, filtering options are easier and cheaper to implement. Therefore, these systems will not be discussed further.

Residential pellet systems are with 465 000 installed units well established in Germany. Due to the availability of sustainable pellets in Germany, predictions estimate that one million residential pellet systems will be installed by 2040 [65]. However, this estimation strongly depends on the regulatory framework. There are a variety of different systems, ranging from small units designed to heat single rooms to pellet systems for large apartment buildings. Automation and a standardized fuel quality enable efficiencies over 90 % [66]. Pellet systems avoid CO_2 emissions and rely on local or regional fuel [67]. Compared to heat pumps, pellet systems have the advantage of high flow temperatures that enable the use of existing heating systems.

Particulate matter emissions from pellet heating systems originate from unburned hydrocarbons as well as from alkali species [66]. Due to advanced and automated combustion systems as well as uniform fuel quality, fine particle emission from unburned hydrocarbons can be drastically reduced compared to other residential systems. In sophisticated pellet systems, inorganic fine particle emissions are the most relevant particulate matter emissions. Additives can reduce these inorganic fine particle emissions. The simplest way of additive introduction is the inclusion in the pellets. Huelsmann et al. found a significant reduction of fine particle emission by the addition of kaolin to wood pellets [68]. The inclusion of additives in wood pellets is protected by a patent of the FireStixx Holz-Energie GmbH (Essenbach, Germany) [69]. Since investment costs, maintenance, and reliability are crucial in household applications, more complex additive introduction systems are unlikely to be economically feasible.

Figure 2.1 shows the three most common commercial combustion systems for solid biomass. The combustion chamber of grate, fluidized bed, and suspension combustion systems are shown. The grate and suspension firing systems also include the heat exchanger section. The logarithmic power scale roughly categorizes existing combustion systems.

Grate firing units typically feed larger bulk biomass with a mechanical stroker onto the grate. The grate distributes the fuel in the combustion chamber. The biomass burns as it moves down the grate, and the ash is collected at the end. Primary combustion air is supplied via the grate. The primary air is also used to cool the grate. Some grate systems have additional water cooling systems integrated in the grate. Above the grate, secondary air is introduced into the combustion chamber. The secondary air is crucial for complete combustion and emission reduction. After combustion, the flue gases enter the heat exchanger section. [70]

Compared to suspension and fluidized bed combustion systems, grate furnaces usually have a lower electrical efficiency of approx. 30%, due to the challenging fuels that are burned in grate-firing systems. [71]. The advantages of grate firing systems are their very high fuel flexibility and the low investment and operating costs compared to other firing systems [72]. The production of heat can compensate for the low electric efficiency of grate firing systems. The smaller dimensions of the combustion systems enable a decentralized heat and power generation [73].

In grate firing, only 10-30% of the fly ash is entrained in the flue gas [74]. Thus, fine particle and deposition formation are less severe than in suspension-fired units where typically 80-90% of the fly ash is entrained in the gas phase. Since biomass fuels typically have low ash melting points due to the high content of potassium, grate firing systems can face problems with fuel bed agglomeration [70].

Fluidized bed combustion systems use a bed material consisting of small solid particles, usually silica sand. The fuel is added to the bed and combusts in the bed and in the gas phase. The

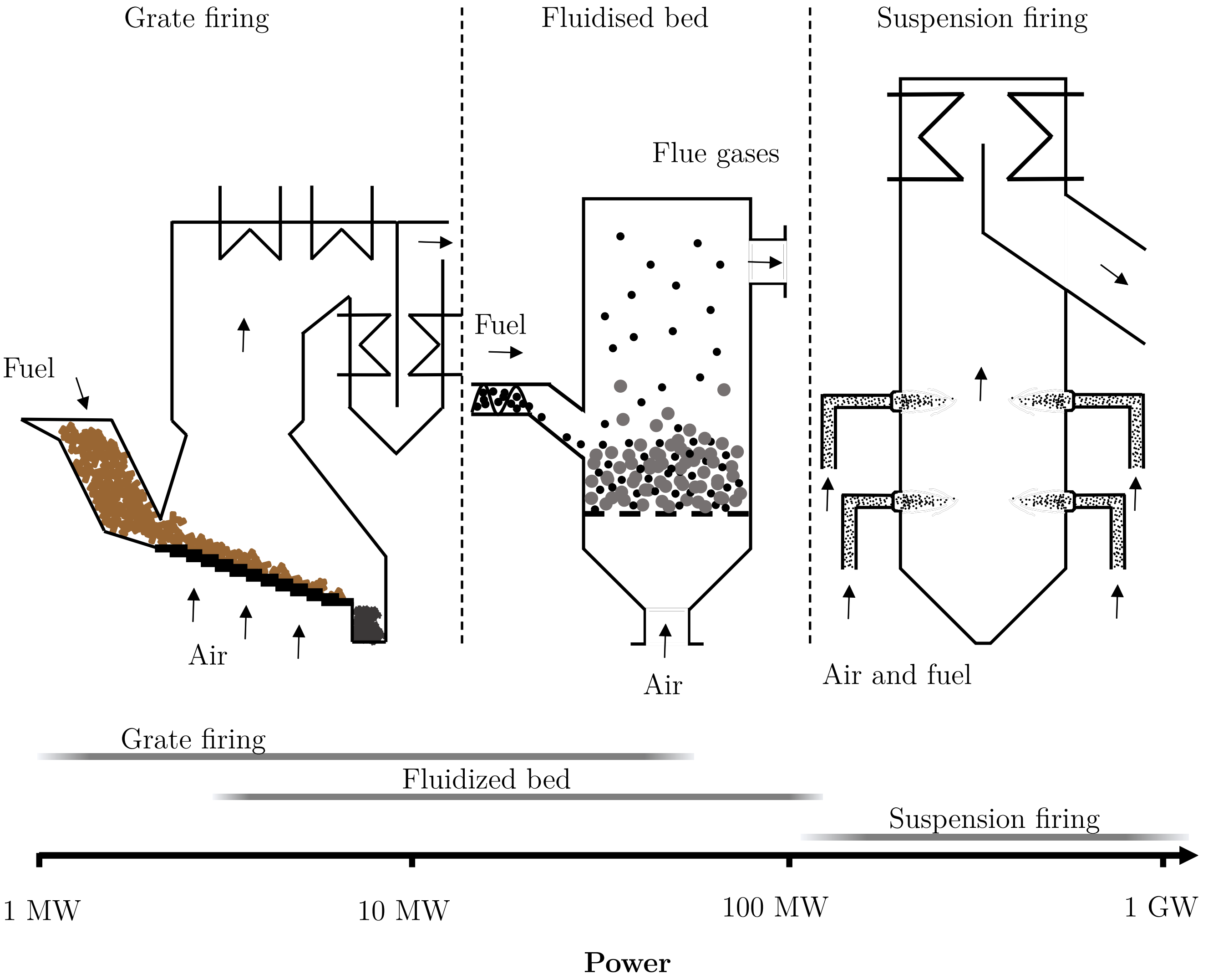


Figure 2.1: Overview and power classification of commercial combustion systems for solid biomass. Adapted from [9, 70, 75–77]. Published in paper V [27].

interaction of the fuel and the bed material affects the combustion, which is characterized by a homogeneous temperature profile. The primary air is supplied by nozzles below the bed and flows through the bed material. This flow leads to the fluidization of the bed material. The degree of fluidization varies depending on the flow velocity of the air. At low velocities, the bed material is kept in suspension, and only few particles are transported out of the bed. In this bubbling fluidized bed setup, there is a distinct boundary between the bed and the gas phase. A bubbling fluidized bed (BFB) system is shown in figure 2.1. At higher flow velocities, the bed particles are carried out further, and a defined bed surface disappears. Since a large portion of the bed material is carried out, a recirculation of the bed material is required. A circulating fluidized bed (CFB) system uses a cyclone to separate the entrained bed material from the flue gas in order to recirculate the bed material. [78]

Secondary air is supplied on top of the bed and in the freeboard zone. Electric efficiencies of fluidized bed systems are in the range between 30% and 40% [79].

The advantages of fluidized bed combustion are the high fuel flexibility, the low NOx emissions due to the low temperatures, and the relatively high efficiencies. Challenges are the high capital

and operating costs as well as bed agglomeration [72].
The major ash-related problem in fluidized bed biomass combustion is bed agglomeration. Molten ash phases cause the bed material to clump, which can lead to clogging and partial or complete defluidization. [80]

In **suspension firing systems**, pulverized fuel is pneumatically blown into the combustion chamber by the primary air. Due to the small particle size, the fuel particles react quickly. The combustion is characterized by high temperatures, good mixing, and short residence times. The high power density of suspension firing systems, originally designed for coal combustion, enables large-scale power plants since multiple burners can be grouped in one combustion chamber. The fuel quality, in general, and the particle size, in particular, are important to ensure a stable operation. [81]
A major challenge in using biomass is fuel preparation. Biomass has a fibrous rather than crystalline structure, which makes it more difficult to grind than coal. For combustion, biomass must be pulverised to particle sizes well below 6 mm. Additionally, the moisture content of the fuel must be very low compared to the other two combustion systems [70, 81, 82].
High temperatures and good mixing enable high electric efficiencies of up to 46–48% [71]. Moreover, suspension firing systems are able to adjust the load quickly [81]. Low fuel flexibility, extensive fuel preparation, and, compared to the other two combustion systems, the highest operating and capital costs are challenges of suspension firing systems [72].
Furthermore, suspension firing systems face problems with slagging and fouling of power plant surfaces and heat exchangers. The deposits reduce the heat transfer rates and can lead to high-temperature corrosion. [10, 13]

Overall, the combustion conditions in general and the temperature range in particular differ between the different types of power plants. This affects the release of ash-forming elements and the composition of the gas phase. A more detailed description and the temperature profiles of the commercial combustion systems are given in paper V [27].

2.3 Alkali Release

In combustion processes, alkali metals are released into the gas phase during devolatilization and char oxidation [39]. The release strongly depends on the temperature, but numerous other factors influence the release behavior. Therefore, alkali release from various biomass feedstocks occurs over a wide temperature range [83]. The alkali metals sodium (Na) and potassium (K) generally follow a similar release behavior and cause similar problems. However, due to its low concentration, sodium usually accounts for less than 3% of the fine particle and deposition formation during the combustion of solid biomass [9]. Hence, only the release of potassium is discussed in detail. This section first summarizes literature data on potassium release and discusses different analytical methods for determining potassium release. Afterward, the mechanism of the potassium release is discussed, and existing models for the alkali release are briefly introduced. Parts of this section have been published in paper II [25].

"Potassium is released over a wide temperature range. Van Lith et al. report the commencement of potassium release at around 500 °C [84, 85]. A similar potassium onset temperature is predicted by the model of Cao et al. [86], while Mason et al.'s compilation of published data suggests that release begins at around 700 °C [87]. All published data report a continuous release up to 1300 °C and indicate that not all of the potassium is released to the gas phase at this temperature [83–85, 87].

Figure 2.2 shows a compilation of published data on the relative potassium release over temperature for various types of biomass [84, 85, 88–93]. The experimental conditions applied by the groups vary, with some groups investigating several sets of parameters. Moreover, multiple types of biomass are analyzed. The curves shown in the figure represent the average of all measurements by a single group. The slightly negative potassium release detected at low temperatures in the experiments by Misra et al. result from methodological inaccuracies [91]. The gray curve is a function fitted over all values and indicates the overall trend.

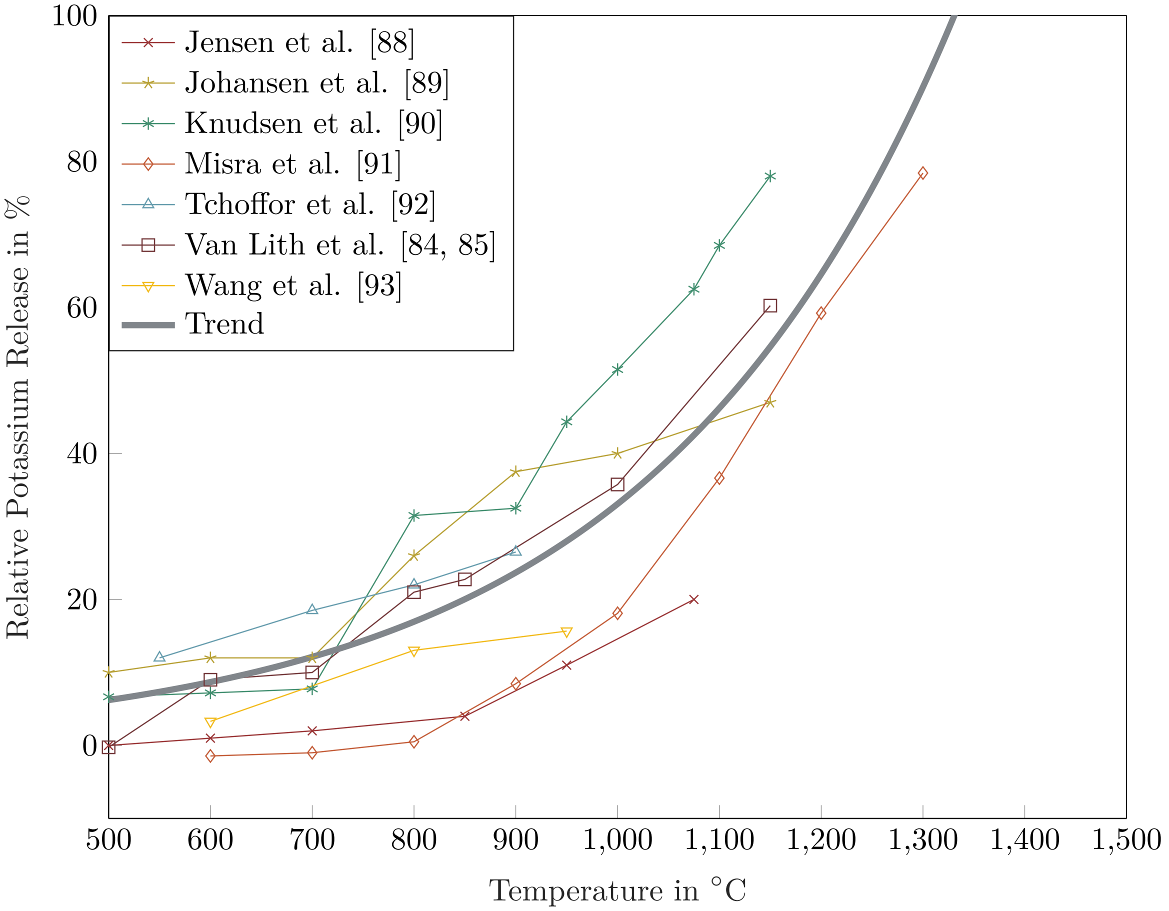


Figure 2.2: Average relative potassium release for various biomass samples. The experimental conditions vary between the different papers. The shown values are averages of all measured biomass samples of the cited groups. Adapted from [84, 85, 88–93]. Published in paper II [25].

While the amount of potassium released is greatly dependent on the potassium concentration, release occurs in a similar temperature window independently of the concentration. An increased heating rate may result in potassium release at lower temperatures. Okuno et al. suggest that a faster temperature increase suppresses intraparticle secondary reactions by reducing the residence time of volatiles. The release-promoting influence of the heating rate is particularly significant with rapid heating. The opposite trend can be observed with slow heating or long exposure times. [94]

Exposure time has a significant effect on potassium release. Okuno et al. found that exposure to relatively high temperatures can result in a small but continuous release of potassium. This exposure can result in a complete release at temperatures at which only a fraction of the potassium is released with shorter exposure times [94]. However, the influence of heating rate and exposure time also depends on the biomass and the setup. The atmosphere can influence potassium release in multiple ways. Carbon dioxide (CO_2) inhibits it [95], while French et al. suggest that the presence of water vapor shifts the chemical form of the released potassium, thereby increasing the release temperature [96]. Oxygen promotes the inclusion reactions of potassium in aluminum and silicon compounds. This can increase the amount of potassium retained in the ash. However, the release-suppressing effect of oxygen is more relevant in laboratory investigations, since oxygen can increase the temperature in combustion or gasification applications [12]. These interdependencies between the investigated biomass, experimental setup, and precise composition of the atmosphere make clear statements about the influence of just one factor difficult. Generally, it is hypothesized that reducing atmospheres can lead to a stronger release of inorganics, since the equilibrium partial pressures of reduced inorganic species such as Si, Zn and Pb are often higher than their oxidized counterparts [39]. Other elements present in the biomass can directly or indirectly affect the release behavior of potassium. Chlorine content can either be an indicator of the presence of potassium chloride or result in the formation of potassium chloride during thermal conversion. Since potassium chloride is relatively volatile, chlorine is generally associated with promoting potassium release [12, 95, 97, 98]. Aluminum and silicon oxides can capture potassium and bind it in temperature-stable compounds [12, 21]. As a result of this inclusion reaction, the aluminum and silicon content can directly inhibit the release of potassium [99]. Since silicon favors reactions with magnesium and calcium over potassium, the concentration of these alkaline earth metals can indirectly promote the release of potassium [94]. Phosphorus is also reported to retain potassium in the ash. Grimm et al. found a significant reduction in volatile potassium species for increased phosphorus contents in the biomass samples [100] . The multitude of factors influencing potassium release behavior illustrate the difficulty of isolating the impact of any single factor. Comparing results can be difficult too, since the experimental conditions and sample properties need to be assessed. Moreover, drastically varying results and partly contradictory views in the literature make general assumptions difficult and highlight the need for detailed experimental data." [25]

Experimental Setups for Alkali Release Measurements

The release of alkali metals from coal has been extensively analyzed, e.g., in [12, 101–103]. Due to differences in concentration and matrix effects, the measurement techniques used for coal analysis need to be adapted, but they can also be applied for the analysis of biomass. Since the potassium concentration in biomass is usually much higher than the sodium concentration, the focus of the analysis of biomass is shifted to potassium. Even though some groups cited below have analyzed both coal and biomass with a similar setup, only examples of biomass analysis are given in the following section. This section has been published by the author in paper II [25].

"In order to compare the different measurement methods for release from biomass samples, it

is important to distinguish between the experimental setup for release or evaporation and the analytical method for determining the concentration of compounds or elements. The simplest release setup is an electrically heated furnace as used by Jensen et al. [88], Johansen et al. [89], Knudsen et al. [90], as well as van Lith et al. [84, 85]. The concentrations before and after the furnace are determined with an acid digestion [104] and subsequent analysis by ICP-OES [84, 85, 89, 90] or inductive coupled plasma-atomic emission spectroscopy (ICP-AES) [88]. The release is determined by comparing the initial concentration to the concentration after the furnace. Misra et al. [91] and Wang et al. [93] conducted similar batch experiments with TGA systems and analyzed their samples using ICP-OES. All these experimental setups have low heating rates, long exposure times and that no online measurements of the gas phase are performed in common.
Bläsing et al. [105, 106] and Dayton et al. [107] monitored the gas phase at the end of an electrically heated furnace with an MBMS. This method is capable of analyzing molecular concentrations and not just elements, but enables only a qualitative analysis because it cannot be calibrated for an accurate quantitative analysis.
Porbatzki [108] monitored the released molecules in the gas phase by Knudsen effusion mass spectrometry (KEMS). The method, capable of analyzing the temperature resolved release of all relevant molecules, is limited to qualitative analysis and restricted by the maximum temperature in the Knudsen cell.
Sommersacher et al. [109, 110] analyzed the gas phase of a macro TGA with an inductively coupled plasma mass spectrometer (ICP-MS). This very sensitive setup allows a temperature resolved qualitative analysis of the elemental release.
The group around Jones investigated the release behavior in various publications in the same single particle combustion set-up [87, 111–114]. A biomass particle is suspended into the flame of a Meker burner and exposed to temperatures of about 1600 °C. The radiative emissions associated with potassium release are recorded by two photodetectors. Thereby, the qualitative potassium release can be analysed over the exposure time. Due to the high heating rates and maximal temperatures, this set-up comes closest to real combustion conditions. However, the experimental technique is not suitable for lower temperatures, so it is not possible to determine the release temperature. Moreover, quantitative analysis is not possible.

As shown, there are a variation of different measurement techniques for the release of inorganic elements from biomass. However, the experimental parameters can differ significantly so a direct comparison can be difficult. This needs to be considered when evaluating figure 2.2 that summarizes the results of all quantitative measurements mentioned above." [25]

Mechanism and Model for Alkali Release

The reaction pathways and chemical composition of the released species are important for understanding alkali release and inclusion into additives. This subsection describes the release pathways and mechanisms, while approaches to mathematically quantify the release are described in the subsections on alkali release models.

Generally, most potassium is released as KCl, KOH, K_2SO_4, and in elemental form. The possible release and subsequent reaction paths developed by Johansen et al. are shown in figure 2.3 [89].

Similar to the release and reaction pathways postulated by Van Lith et al. [84, 85], the model by Johansen et al. involves multiple release and transformation steps over a wide temperature range. While these models highlight possible reaction pathways, neither the concentration of a certain species nor the release temperature can be predicted [25, 89]. As shown in figure 2.3, potassium forms stable silicate bounds. Since these silicates remain solid under combustion conditions, the compounds are considered a stable product in all release models in the literature. The interaction with the ash silicates is the same reaction as with aluminosilicate-based additives and is described in detail in section 2.5.
The group around Fathei identifies eleven reaction pathways in their experiments and model on the potassium release from biomass [25, 95, 98, 115–118]. Anca-Couce et al. propose a simplified model that focuses on the release of KCl and KOH with the aim to quantify the release in addition to qualitatively describing the potassium release [119]. Huang et al. [120] and Liu et al. [121] identified KCl, KOH, and elemental potassium as the most relevant potassium species in their release mechanisms.

While there are different proposed mechanisms for the release in literature, it is generally agreed that potassium is released as KCl, KOH, K_2SO_4, and elemental potassium. However, the amount and ratio of the released species are hardly quantified in the literature. Potassium undergoes complex changes in all combustion stages, and the release pathways strongly depend on the biomass composition and conditions like heating rate and atmosphere. Therefore, it is impossible to accurately predict the potassium release based on reaction or release mechanisms.

For CFD simulations and other calculations, the alkali release must be mathematically quantified and modeled. The approaches reported in the literature to model alkali release are limited. The overview given by Kerscher [12] is extended with the latest publications in the field. As Kerscher pointed out, most models use a first-order Arrhenius approach to model the release [12]. The Arrhenius equation relates the rate constant (k) to the activation energy (E_A), the temperature (T), and a pre-exponential factor (A) [12, 122, 123].

$$k = A\, e^{\frac{-E_A}{R\,T}} \tag{2.3}$$

Fathei et al. used this Arrhenius approach to model the overall potassium release rate ($\dot{r}_K$) [115, 116].

$$\dot{r}_K = \frac{dm_K}{dt} = m_K\, A_K\, e^{\frac{-E_{A_K}}{R\,T}} \tag{2.4}$$

The subscript K indicates potassium, but the same model could be used for sodium (Na). m_K refers to the potassium bound in the biomass. In a more complex model by the same group, the potassium release rate is broken down into nine submodels that model the release of one particular potassium species [117]. The release pathways that involve a chemical reaction or transformation are modeled with an Arrhenius approach. The evaporation of KCl, K_2SO_4, and K_2CO_3 are modeled with evaporation rates postulated by Knudsen et al. [90]. Qu et al. compared the model to experimental data and found good agreement [118]. The release model by Cao et al. also assumes first-order reactions and utilizes least-square fitting to minimize the difference between the model and experimental data by Knudsen et al. [86, 90, 124]. Anca-Couce et al. employ an Arrhenius

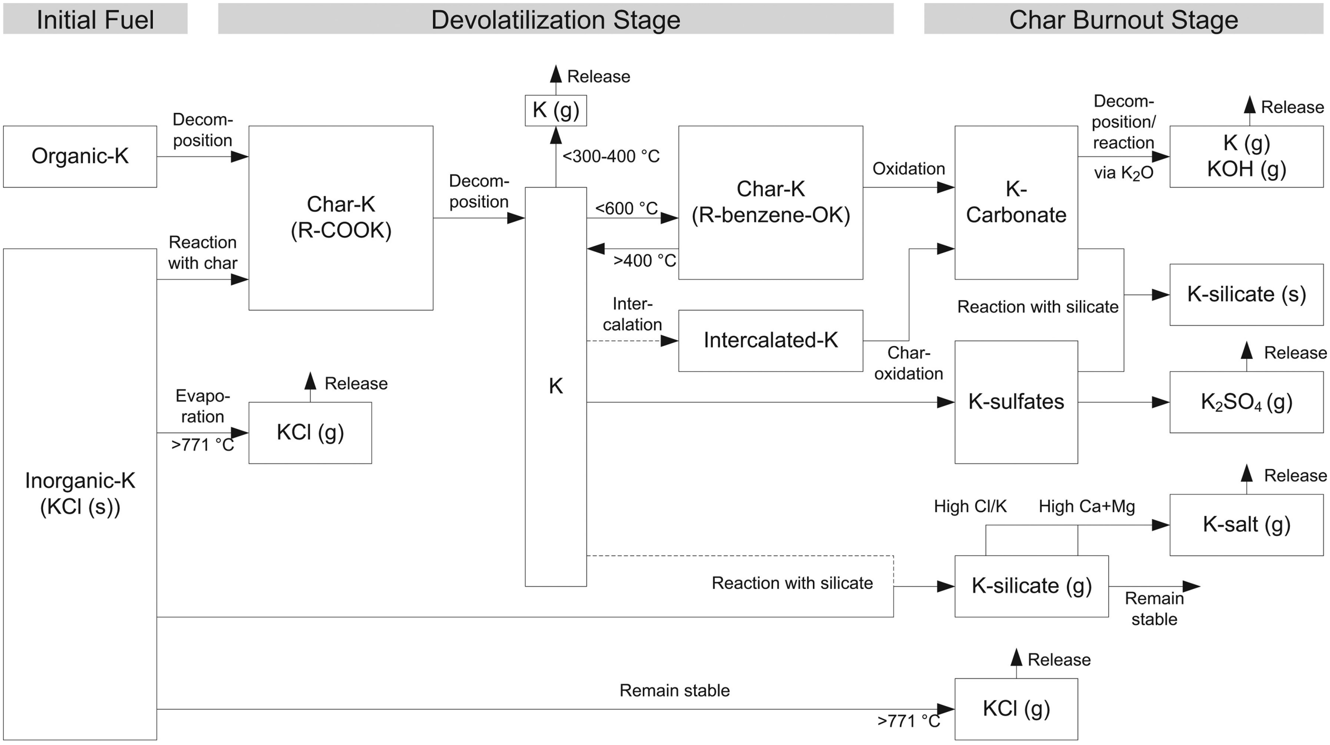


Figure 2.3: Possible reaction paths and release mechanisms of Potassium during the combustion of biomass. Developed by Johansen et al. with special emphasis on the combustion of annual crops [89]. Reprinted with permission from [89]. Copyright 2011 American Chemical Society

approach and focus on the different release pathways during each stage of combustion [119]. An Arrhenius approach is also used to model potassium release from biomass or coal in the release model of Akbar et al. [125]. Due to the high silicon and aluminum contents in coal, Akbar et al. also model the inclusion in alumino-silicates. This approach could potentially be used to model the influence of additives in the fuel.

In general, experimental data on alkali release are limited. This is a major challenge in developing a mechanistic model, as the many factors that influence potassium release are not adequately addressed in the existing experimental data. A more complex model might not be more accurate than a simple model if it is fitted to the same experimental data. The interested reader is referred to Kerscher for models that consider diffusion and reaction progress [12]. In summary, the alkali release is dependent upon a number of influencing factors and, therefore, requires individualized analysis for each biomass type.

2.4 Fine Particle and Deposition Formation

This section outlines the formation of fine particles and depositions. Both phenomena go back to the condensation of alkali vapors. First, the formation and the health effects of fine particles are discussed. Then, the formation of depositions and their impact on the power plant performance are discussed in detail.

Fine Particle Formation

In general, a small fragment of a liquid or solid substance with a defined boundary surface is considered a fine particle. PM is in some sources used as a synonym and in others used as a term to describe fine particles that are entrained in a gas flow [126–128]. Here, particulate matter is used to describe airborne fine particles. Since these fine particles can differ significantly in size, they are further classified. $PM_{2,5}$ describes particles with an aerodynamic diameter of less or equal to 2.5 µm and PM_{10} describes particles with an aerodynamic diameter of less or equal to 10 µm [127, 128]. The health impact of PM depends significantly on the particle size because smaller particles can penetrate deeper into the respiratory system and even enter the bloodstream. The impacts of PM exposure range from cardiovascular diseases and cancer to premature death [129]. Therefore, not only the emissions of firing systems but also the overall $PM_{2,5}$ and PM_{10} concentration in ambient air are regulated [128, 130].

Fine particle emissions can originate from organic or inorganic compounds. The organic fraction resulting from the condensation of hydrocarbons is called soot. Soot formation is a complex process because it involves numerous hydrocarbon species and depends on fuel properties and combustion conditions. However, under the right conditions, soot can be completely oxidized. Therefore, soot emissions can be controlled in properly designed and operated combustion systems [131, 132]. Soot is not discussed further in this work because the focus is on inorganic particles.

The pathways for inorganic particle formation during solid biomass combustion are shown in Figure 2.4 [128]. During combustion, the minor and trace elements are partly released into the gas phase and form inorganic vapors. Some of these inorganic vapors, most importantly potassium compounds, have high condensation temperatures, so they condense when the flue gas is cooled. This condensation can lead to the nucleation of ultrafine particles or heterogeneous condensation on existing particles and surfaces. Via coagulation and agglomeration (ultra)fine particles can form larger fly ash particles [9, 39, 53, 128]. The formation of inorganic particles follows complex pathways and depends on fuel characteristics and combustion conditions [132]. Once inorganic particles are formed, they can only be filtered out of the flue gas. Further oxidation is not possible. Therefore, the release of potassium species and the presence of condensable potassium species are critical. For the mitigation of fine particle formation, either the release of potassium must be suppressed, or the condensable species must be captured by temperature-stable compounds that are larger than 10 µm before fine particles can be formed.

Fine particle emissions are a challenge in small-scale combustion systems because these systems usually lack adequate after-treatment systems. In power plants, electronic filters are used to prevent the emission of fine particles. With filter efficiencies of up to 99 wt.%, the emissions of large particles can be reduced to unproblematic levels. However, filter efficiencies are lower for very small particles with diameters below 1 µm [133–135].
The fine particle and the deposition formation follow similar pathways. However, the focus of this work is on mitigating the formation of depositions, as this is much more relevant in power plants.

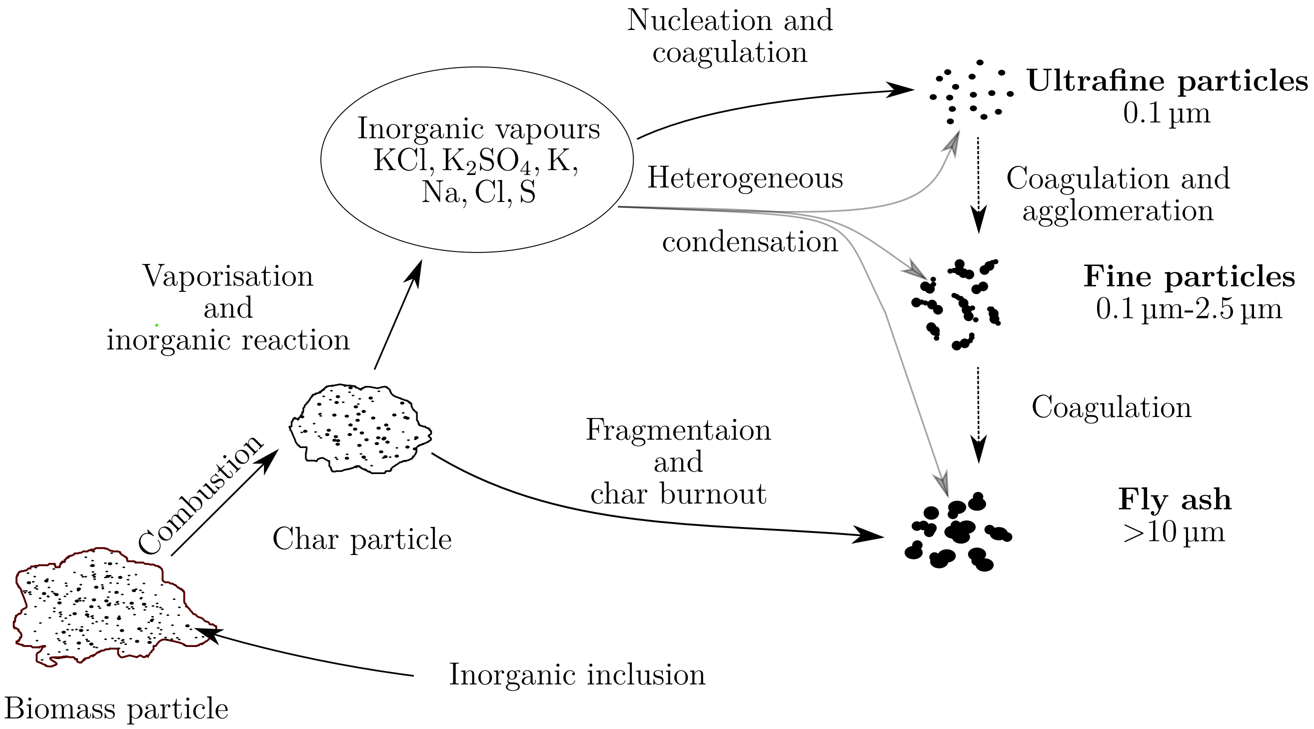


Figure 2.4: Particle formation during the combustion of solid biomass. Adopted from van Loo, Kaltschmitt and Frandsen [9, 39, 53, 128]. Published in [128].

Deposition Formation

The four main mechanisms, condensation, thermophoresis, inertial deposition, and chemical reaction, cause deposition. Each mechanism has its own timescale. In addition, the operating conditions and the boiler geometry strongly influence the deposition formation [136].

Condensation occurs when the temperature of a heat-exchanging surface is lower than the condensation temperature of flue gas species. In biomass combustion systems, these species are inorganic vapors, mainly alkali compounds. Among the volatile species, alkali compounds have relatively high condensation temperatures and are present in relatively large quantities. Hence, alkali compounds like alkali chlorides (KCl, NaCl), alkali hydroxides (KOH, NaOH), alkali sulfates (K_2SO_4,Na_2SO_4), and alkali carbonates (K_2CO_3, Na_2CO_3) are mainly responsible for condensation phenomena. In addition, volatile heavy metal compounds can condense in cold spots. Condensation occurs not only directly on the heat exchanger but also on fly ash particles and pre-existing deposits. [13, 128] Inertial deposition build-up results when larger fly ash particles ($d_p > 10\mu m$) cannot follow the streamlines around an obstacle. Due to their inertia, these particles impact on the surface. Larger fly ash particles have higher inertia and are, therefore, more likely to impact on heat exchanger surfaces. In many applications, inertial deposition is the most dominant deposition formation mechanism [11]. Inertial depositions only occur on the windward side of heat exchanger surfaces. Thermophoresis is a deposition path relevant for small particles. Thermophoresis describes a force in a temperature gradient field that acts on the particles on top of drag, gravity, and Brownian forces [137]. The force pulls particles from the hot flue gas towards the cooler heat exchanger

surfaces. Even though the phenomena is not completely understood, it must be taken into account when assessing the deposition formation [13].
Depositions, just like fly ash particles, can react with the flue gas. The heterogeneous chemical reactions can lead to sulfation, carbonation, oxidation, or reduction. Moreover, alkali species can be adsorbed by pre-existing depositions similar to the inclusion in additives described in section 2.5. The chemical reactions are significant because they determine whether the depositions grow or detach from the surfaces [11]. Biermann et al. find similar heterogeneous chemical reactions between the flue gas and an additive temporarily deposited on the heat exchanger surfaces [138]. The physical and chemical properties of depositions and the dominant deposition mechanism change over time.

Deposition formation can be simplified into three steps. First, an initial deposition is formed. The initial deposition is formed primarily by thermophoresis and condensation, as the temperature gradient between the blank heat exchanger and the flue gas is highest in the initial stage. The deposition probability of inertially impacting particles is low on smooth, deposition-free surfaces. Deposits formed in the initial stage consist of inorganic vapors with low saturation pressure, mainly potassium compounds [15].
In the next step, the deposition growth, the formation originates mainly from inertial deposition and thermophoresis. The initial layer changes the surface structure, so the deposition probability of inertially impacting particles is significantly increased [10]. Potassium compounds are crucial in this step because they bind fly ash particles together and form a sticky surface [139, 140].
During advanced deposition growth, the temperature difference between the flue gas and the outer depositions is significantly lower. Hence, the temperature difference-driven mechanisms of condensation and thermophoresis are less relevant. At this stage, sintering processes, chemical reactions as well as inertial deposition change the deposition structure and lead to deposition growth. [10]

Alkali compounds, mainly potassium salts, are crucial for deposition formation and growth. In order to limit the deposition formation, the release of the potassium species must be avoided, or the problematic species must be captured by additives as described in the following section 2.5.

Impact on the Power Plant Performance

Depositions are problematic on multiple levels. First, the heat transfer rate is reduced due to the thermal resistance of the depositions [13]. Moreover, the depositions are rich in chlorine so they can cause significant corrosion. High-temperature chlorine corrosion drastically limits the lifetime of power plants, so it needs to be avoided. Problems with high-temperature corrosion generally increase with the temperature [10]. A common way to reduce deposition formation and limit high-temperature corrosion in biomass-fired power plants is to reduce the maximum steam temperature [10, 39]. However, this measure drastically reduces the electrical efficiency. As a result, the efficiency of biomass-fired power plants is reduced by two factors: directly by the limited heat transfer through depositions and indirectly by the measures to limit deposition build-up and corrosion.
Further techniques to limit the operation problems include the use of resistant material, the removal of problematic species before the combustion, additives, mixing with less problematic fuels, or

advanced soot-blowing strategies [39]. However, all these measures increase the cost of biomass combustion.

The prediction of deposition and corrosion problems in real power plants is challenging and complex. Various factors, such as the biomass composition, the atmosphere, the temperature, and the flow conditions in the boiler, need to be considered [10, 11]. To reduce the complexity, various fuel indices have been developed to assess the fouling and the slagging tendencies of a fuel.
"The alkali index puts the amount of alkali oxides in the fuel in relation to the lower heating value ($\frac{K_2O+N_2O}{LHV}$). Based on experience, thresholds for probable and certain slagging are defined [141, 142]. This alkali index for combustion should not be confused with the alkali index for gasification defined by Skawa et al, which is a ratio of the catalytic and inhibitory components of the ash [12, 143]. All indices in this [work] refer to the mass fraction. The base-to-acid ratio is adapted from coal combustion to predict the fouling tendency of a fuel [62].

$$R_{b/a} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3} \tag{2.5}$$

A base-to-acid ratio above 0.5 is problematic for coal combustion [31]. However, as with other indices derived from coal combustion, the applicability to biomass combustion is limited [62, 144]. To overcome this, Niu et al. propose the Cl- and S-ratio that take the most relevant elements for the deposition formation into account [145]. The definition and proposed thresholds are shown in table 2.3.

Table 2.3: Cl- and S-ratio for the prediction of the slagging tendency of biofuels as proposed by Niu et al [145]. Published in Paper IV [26].

	Definition	**Slight Slagging**	**Serious Slagging**
Cl-Ratio	$\frac{Cl+K_2O+Na_2O}{SiO_2+Al_2O_3}$	≤ 1.0	≥ 2.4
S-Ratio	$\frac{S+K_2O+Na_2O}{SiO_2+Al_2O_3}$	≤ 1.0	≥ 1.9

While the Cl- and S-ratio take the most relevant elements into account, the bonding type, the total amount of ash, and the heating value are not considered. All fuel indices aim to provide useful guidelines for fuel selection. However, their accuracy is limited, and no single index can reliably describe the ash behavior for all combustion systems [62].
Another well-established method for evaluating and comparing the slagging and fouling tendencies of a fuel is ash melting analysis [39, 146, 147]. In this analysis, different characteristic deformation temperatures are determined for an ash sample. The focus is placed on the temperature window between the sintering temperature at the onset of ash melting and the melting temperature of the ash [146]. While it is widely accepted that slagging and fouling problems result from low ash melting temperatures, the transfer to real applications and the repeatability of the ash melting analysis can be challenging [146, 148].
Therefore, no laboratory analysis or calculated fuel index can reliably predict the deposition formation problems associated with solid biomass combustion. This is a challenge not only for the selection of suitable fuels but also for the analysis of additives as a measure to mitigate slagging

and fouling." [26]

Overall, alkali species can drastically reduce the efficiency of biomass combustion systems, but the exact impact is difficult to predict based on fuel characteristics.

2.5 Inclusion of Alkali Species in Additives

The problems associated with fine particle emissions and deposition formation, that are described in the previous section, can be reduced or overcome by the use of certain additives. This can increase overall efficiency or reduce the need for additional after-treatment measures. The additive use aims to capture problematic species before they condense and bind them in solid, temperature-stable compounds.

In this section, the inclusion mechanism of alkali species in additives is discussed in detail. First, the fundamental processes regarding sorption are differentiated. Then, different types of additives are discussed with a focus on aluminosilicate-based additives. Finally, the mechanism and the influencing factors on the alkali sorption are discussed, and the challenges for optimizing an additive introduction system are highlighted.

Fundamental Sorption Processes

Sorption processes can follow several pathways that need to be differentiated. Adsorption is defined as a substance becoming attached to a surface [40]. A force field at the surface of the solid reduces the potential energy of the adsorbed molecule, causing it to leave the fluid phase [149]. Hence, adsorption is a surface interaction. If the adsorbed molecule penetrates the surface into the solid phase, the process is considered absorption [150]. Another way sorption processes are categorized is by their bond type [12]. Physical adsorption occurs when molecules interact by noncovalent forces, mainly van der Waals forces supplemented by polarization, field-dipole, and field gradient forces. If the sorptive is bonded to the sorbent in a chemical bond, the process is defined as chemisorption. Chemisorption always involves electron transfer or sharing and is therefore much stronger than physical adsorption [149, 150]. In solid-fluid sorption processes, adsorption is equal to physical adsorption, while absorption is a synonym for chemisorption. It can be difficult to clearly differentiate between physical adsorption and chemisorption. Therefore, processes involving both pathways are referred to as sorption.

Additives

In order to reduce the ash-related problems described in section 2.4, most additives generally aim to reduce the potassium content in the gas phase. The sorption rate and capacity of the additives must be adequate, and the products of the sorption process should be noncorrosive and temperature stable [12].

"Additives have been widely used for the mitigation of ash-related problems. The additives need to be non-toxic, easy to handle, and available in large quantities. The life cycle cost of the additive

systems must be less than that of a potential after-treatment system or the revenue from increased efficiency.
There are multiple additives that at least partly fulfill these criteria. The most common additives are based on sulphur, phosphorous, calcium, or aluminum silicate. The classification is based on the dominant reactive component [151]. Sulphur-based additives reduce the KCl content in the gas phase and have been tested in biomass-fired boilers. While sulphur-based additives reduce corrosion problems, the fine particle formation pathways are just shifted from KCl to K_2SO_4 [152]. Phosphorous-rich additives can react with potassium and reduce the potassium available for initial deposition formation [51, 151]."[26] Added to the fuel, phosphorous-rich additives can reduce the potassium release [153]. "With the ongoing depletion of mineral phosphorous and growing concerns about the anthropologically broken phosphorus cycle, phosphorus might be too precious to be added to a combustion system [51, 154]. Moreover, for certain combustion systems, phosphorus management is soon going to be required [52].
Calcium-based additives can improve the ash melting and sintering behavior. Moreover, by capturing KCl, these additives reduce the fine particle and deposition formation [151]. Since it is known that calcium-based additives react with phosphorous and silicates, it can be difficult to group the additives into one category. Furthermore, some calcium-based additives contain significant amounts of phosphorous [151].
Additives rich in aluminum and silicon can capture alkali vapors and thereby reduce both the deposition and the fine particle formation [151]. Aluminum-silicate-based additives have been extensively tested on lab-scale, [12, 16, 17, 155–162] pilot scale, [18, 19] and large scale conditions [18, 80, 162, 163]. The most prominent aluminum-silicate-based additives, kaolin, halloysite, and CFA, are relatively cheap and available in large quantities. This work focuses on kaolin and CFA as they are the most promising additives for both small- and large-scale applications."[26]

Mechanism of the Alkali Sorption

Kaolin and CFA follow a similar alkali capture mechanism, but there are certain differences. Kaolin is a mined mineral and is, therefore, usually purer than CFA, the composition of which varies according to the fuel and combustion conditions. Moreover, CFA is a product of a high-temperature process and does not undergo the same thermal changes as kaolin when heated. In the following, the alkali capture mechanism of kaolin is described in detail. While some of the initial thermal changes are kaolin specific, the overall capture mechanism is the same for CFA [164, 165]. When exposed to combustion temperatures, water is driven out of kaolin. The thermal transformation affects the main constituent of kaolin, the mineral kaolinite ($Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$). The product of this dehydroxylation process is the amorphous aluminum silicate metakaolinite ($Al_2O_3 \cdot 2\,SiO_2$). Equation 2.6 shows the dehydroxylation reaction that occurs between 450 °C and 650 °C. [166]

$$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O \longrightarrow Al_2O_3 \cdot 2\,SiO_2 + 2\,H_2O \tag{2.6}$$

Upon further heating, metakaolinite forms spinel ($Al_2O_3 \cdot SiO_2$). This transformation occurs above 980 °C. [167]

$$Al_2O_3 \cdot 2\,SiO_2 \longrightarrow Al_2O_3 \cdot SiO_2 + SiO_2 \tag{2.7}$$

At temperatures between 1100 °C and 1200 °C spinel and silicon dioxide (SiO_2) form mullite ($3\,Al_2O_3 \cdot 2\,SiO_2$) [167].

$$3\,(Al_2O_3 \cdot SiO_2) + 3\,SiO_2 \longrightarrow 3\,Al_2O_3 \cdot 2\,SiO_2 + 4\,SiO_2 \tag{2.8}$$

Mullite can also be formed directly from metakaolinite without the formation of spinel as an intermediate product. Above 1300 °C, mullite changes the crystalline structure [168]. There is no agreement on the exact routes of the phase transformation from kaolinite to mulite. There are also variations in the phase change temperatures reported in the literature. Moreover, impurities and trace elements affect the thermal decomposition behavior and may alter the mullite formation routes. [22, 168]

The structure and phases of pure kaolin at high temperatures are complex and difficult to predict. This is even more true for real additives due to their heterogeneity and impurities. Therefore, the following inclusion equation should be regarded as a global mechanism and not as a detailed chemical reaction path. Equation 2.9 shows a simplified inclusion reaction of potassium chloride (KCl) in aluminum silicates. Sodium chloride (NaCl) follows the same inclusion route [12].

$$2\,KCl\,(g) + H_2O\,(g) + Al_2O_3 \cdot xSiO_2\,(s) \longrightarrow K_2O \cdot Al_2O_3 \cdot xSiO_2\,(s) + 2\,HCl\,(g) \tag{2.9}$$

Equation 2.10 shows the inclusion mechanism of KCl in metakaolinite when no water but oxygen is present [169].

$$KCl\,(g) + \frac{1}{2}\,O_2\,(g) + Al_2O_3 \cdot 2\,SiO_2\,(s) \longrightarrow K_2O \cdot Al_2O_3 \cdot 2\,SiO_2\,(s) + Cl_2\,(g) \tag{2.10}$$

Equation 2.11 and 2.12 display the inclusion mechanism of K_2SO_4 and KOH. In contrast to KCl, these potassium species need no oxygen for the inclusion reaction [22].

$$K_2SO_4\,(g) + Al_2O_3 \cdot 2\,SiO_2\,(s) \longrightarrow K_2O \cdot Al_2O_3 \cdot 2\,SiO_2\,(s) + SO_3\,(g) \tag{2.11}$$

$$2\,KOH\,(g) + Al_2O_3 \cdot 2\,SiO_2\,(s) \longrightarrow K_2O \cdot Al_2O_3 \cdot 2\,SiO_2\,(s) + H_2O\,(g) \tag{2.12}$$

Figure 2.5 shows a phase diagram of the inclusion of potassium in metakaolinite at different temperatures. The horizontal axis displays the ratio of potassium oxide to metakaolinite. On the left side is pure metakaolinite. A ratio of K_2O to Al_2O_3+2 SiO_2 of 1 represents the completion of the reactions 2.9 to 2.12. The temperature is displayed on the vertical axis. The phase diagram is based on thermodynamic equilibrium calculations in FactSage 8.0 [22].

Figure 2.5 highlights the complexity of the potassium uptake by metakaolinite. While the thermodynamic equilibrium calculations are based on a closed system and infinite reaction time, they illustrate that the idealized reactions 2.9 to 2.12 only cover a fraction of the actual process because many other species and phases are involved. The already complex uptake is even more complicated in the slag phase, which makes it impossible to describe the inclusion in just one reaction. In

addition, the phases change over temperature, which complicates the inclusion even further because the temperature changes drastically during the combustion and cooling of the flue gas.
As noted above, the inclusion of potassium into additives is very complicated, even for pure metakaolinite and idealized flue gas compositions. Heavy metals and other impurities can significantly alter the alkali inclusion [22]. In addition, material data on phase transitions and reaction rates are limited, so the rate of incorporation cannot be predicted by calculation. However, the main factors influencing the inclusion reaction can be identified.

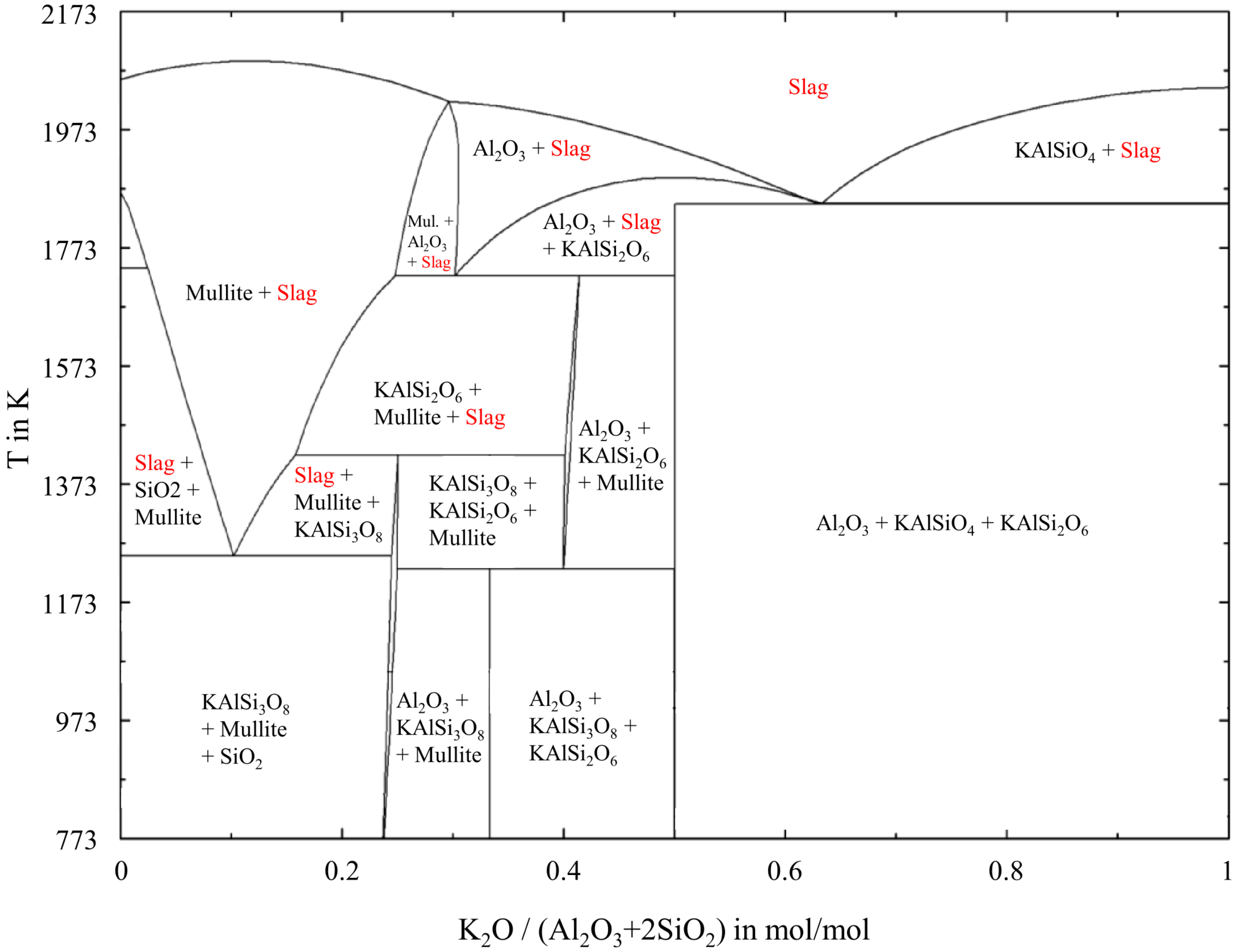


Figure 2.5: Phase diagram of $K_2O/(Al_2O_3+2\,SiO_2)$. Phases with slag occurence are marked in red [22]. Reprinted from [22], with permission from Elsevier.

Influencing Factors of the Alkali Sorption

The residence time of the additive is limited in combustion systems, so the actual alkali uptake can be limited by either the capture rate or the capture capacity. The sorption rate and capacity are additive-specific, and trace elements can significantly change the additive behavior [17, 22].
The temperature generally reduces the maximum uptake capacity of aluminum-silicate-based additives but has a positive direct influence on the inclusion rate [21, 22]. However, once the additive starts to melt, the surface area is decreased, which significantly reduces the inclusion rate [16, 16, 19]. This effect varies drastically between additives. Kaolin has a relatively high initial

surface area, which is reduced by melting processes. CFA, on the other hand, is a product of a high-temperature process with a low initial surface area that stays relatively constant [19]. The change in equilibrium of the potassium compounds is another indirect effect of temperature on capture rate and capacity. This is because the partial pressure and the type of the alkali species strongly affect the sorption rate and capacity. De Riese et al. found that KOH sorption is much quicker than the sorption of KCl or K_2SO_4 [21]. At higher temperatures, the thermodynamic equilibrium of potassium species is shifted from KCl and K_2SO_4 towards KOH [10, 165].
The loading of the additive also influences the sorption rate because saturation effects can reduce the uptake [17]. Moreover, the atmosphere in the reactor influences the sorption rate and capacity [101]. The final alkali uptake by the additive depends on the residence time in the reactor [15].

The effect of each factor is difficult to isolate because they influence each other. Additionally, in combustion applications, temperature, surface area, loading, and gas phase composition are constantly changing, which is another challenge in developing a mechanistic model of alkali sorption.

Additive Introduction

"There are generally two ways of introducing the additive to the combustion system. The additive can either be premixed with the fuel or blown separately into the combustion chamber. Premixing is simpler and ensures maximum residence time, but exposes the porous additive to the maximum combustion temperature. Melting and sintering of the additive reduces the specific surface area, which can drastically reduce the [overall] reactivity. Injection into the flue gas stream allows the optimum temperature window to be selected to avoid melting and sintering temperatures. However, premixing is easier and cheaper to implement, especially in existing combustion systems. Moreover, the additives have an ash-stabilizing effect in fixed bed applications. In order to link the release-inhibiting and ash-stabilizing effects of additives, this work focuses on premixed additive and fuel blends.
Multiple studies show that aluminum-silicate-based additives increase the temperature stability of biomass ash [157, 170, 171]. Due to the use of different procedures for the determination of ash melting temperatures, it is difficult to compare exact values. However, Sommersacher et al. found that adding kaolin to straw increased all characteristic ash melting temperatures from the shrinkage starting temperature to the flow temperature. Depending on the kaolin concentration, the ash melting temperatures were increased by up to 550 °C. Increasing the kaolin concentration to 1 wt.% and 4 wt.% significantly increased the stability. A further increase in the additive concentration to 7 wt.% kaolin hardly changed the ash melting behavior compared to the 4 wt.% sample [170]. Steenari and Lindqvist found consistent results for 4 wt.% of kaolin and dolomite addition in rape, wheat and barley [171]. Roberts et al. generally agree on the mechanism and found similar results for kaolin and coal fly ash but observed a decrease in the ash melting temperature for a blend of 5 wt.% kaolin and white-wood pellets [157]. The general mechanism of the ash-stabilizing effect of aluminum silicates by dilution and alteration of the chemical structure is well understood. Steenari and Lindqvist proved that potassium is incorporated in aluminum silicates [144, 171]. However, the available data are too limited to make reliable predictions about optimal additive concentrations."[26]

Several studies examine the influence of mixing additives with the fuel on the fine particle and deposition formation [114, 153, 161, 170, 172, 173]. "Sommersacher et al. found that significantly less potassium is released into the gas phase when kaolin is added, in addition to a more stable ash melting behavior. Potassium is almost completely retained at kaolin concentrations of 4 wt.% or more for temperatures below 1200 °C. As a result, Sommersacher et al. assume a drastic reduction in aerosol emissions [170]. Similar results were obtained by Clery et al., who observed a retention of 70 % - 100 % of potassium in the ash for temperatures ranging from 550 °C to 1150 °C if CFA is added to the fuel. Moreover, during single particle combustion at approx. 1300 °C, the potassium release analyzed by atomic emission spectroscopy was significantly reduced. The high additive concentration in this work stands out because up to 25 wt.% of CFA was added to the fuel. Even at these high concentrations, fractions of potassium are released into the gas phase at higher temperatures, indicating that it is not possible to suppress the potassium release completely [114]. Liu et al. investigated the potassium release from poplar with different aluminum and silicon-based additives during single particle combustion by laser-induced breakdown spectroscopy (LIBS). A significant reduction in the gas phase concentration of potassium was observed for an additive concentration of 3 wt.%. The investigated additives silica, alumina, kaolin, and mica achieved inhibition efficiencies exceeding 65 %, with the natural minerals kaolin and mica being more effective than pure silica and alumina. The results highlight the inclusion of potassium into both aluminum-silicon networks. In addition, the intensity of potassium release is reduced by the additives, and release occurs over a shorter range, indicating a shift in release temperatures. [173]" [26]

Injecting additives to the flue gas is also well established [18, 163, 167]. Nowak Delgado added CFA during the combustion of wood in a 120 kW pilot-scale pulverized fuel combustion system and found a significant reduction in fine particle emissions [18]. The use of additives has also been successfully tested in large-scale suspension-fired combustion systems [163, 167]. The additive can be blown into the combustion chamber with the air or separately. Biermann et al. found that additives loosely deposit on heat exchangers and other surfaces [138]. This way, the residence time of the additive in the boiler is significantly increased, and the additive is precisely where it needs to inhibit the formation of sticky depositions [138].

Overall, the choice of the right additive and introduction system is a complex task, depending on the fuel and the combustion system. The optimal amount and operation strategies need to be assessed for every additive and fuel. Since the experimental data are limited and the inclusion process is not understood in detail, further experimental studies are necessary.

3

Research Gap and Objectives

As shown in the previous chapters 1 and 2, there has been extensive research in the field of alkali release from biomass and capture by additives. However, data on the release behavior is still lacking, and understanding of release pathways is limited in detail. In the following, the research objective of this thesis is described and the aim of the experiments is explained in detail.

Definition of the Research Objective

The objective of this thesis is to extend the existing understanding of the release of inorganic elements from biomass with a focus on alkali compounds. Of particular interest is the influence of additives on the release behavior and the variations in the release behavior between different biomass types. This thesis aims to describe the release pathways of alkali compounds and how various factors influence the release. In addition, the database for process modeling is extended by temperature-resolved data of various biomass samples. By linking experimental results and process data of existing combustion systems deposition mitigation strategies are evaluated.

Release Experiments and Release Mechanism

The focus of the release experiments is the quantitative assessment of alkali release to the point where all alkali compounds are in the gas phase. In addition to the alkali metals, the release of other minor and trace elements is investigated to analyze the potential chemical bonds of the alkali species in the gas phase. A detailed description of the objectives of the release experiments is listed below. The overreaching objective is to apply the laboratory release experiments to combustion systems.

- First, a stable method for the analysis in the ETV-ICP-OES system is developed. In the literature, ETV-ICP-OES systems have been successfully used for the quantitative analysis of liquid and solid samples. In these publications, the temperature measurements in the ETV were only used to ensure a sufficiently high temperature for a complete release. The few publications that take the temperature into account measure the release only qualitatively and not quantitatively. Therefore, a method that can establish an accurate link between temperature and quantitative analysis of the sample must be developed and validated.

- The existing experimental data in the literature are limited to temperatures at which some alkali compounds remain solid. The goal of the ETV measurements is to continuously measure the release from a wide range of biofuels until all alkali compounds are released. Even though the heating rate in the ETV-ICP-OES is slower than in supsension combustion systems, it is higher than in many experimental setups reported in the literature. The high experimental temperatures of up to 2400 °C enable an analysis of compounds with low volatilities. This allows all potassium species to be analyzed, even those in temperature-stable compounds or initially bound by additives.
- In most experimental setups in the literature, it is not possible to distinguish between released species and products of secondary gas phase reactions. Since the released species in the ETV are rapidly diluted and cooled, the system enables an analysis of the released elements. The simultaneous measurement of multiple elements enables a qualitative analysis of the chemical form in which the potassium is released. The experimental data are analyzed to extend the existing potassium release mechanism. In addition, the differences between release species and secondary gas phase reaction products are highlighted by comparison of the experimental data with literature data.

Link to Thermochemical Conversion Processes

The overall goal of this work is to help improve biomass combustion processes. On the one hand, a deeper understanding of the release mechanism of fine particle and deposition-building species can help to solve design and operational challenges in combustion systems. On the other hand, the analysis of unconventional biomass types and additives can help to extend the available fuel options. With this twofold approach, the results of this thesis can be applied to various combustion systems. Moreover, the results are also applicable to gasification and pyrolysis applications. The specific objectives for this link to real applications are listed below.

- The influence of additives on the ash melting behavior has been analyzed in literature. Linking the shift in the ash melting behavior and the release behavior helps to prove the reaction pathways and to gain a deeper understanding of the processes involved. Moreover, blending additives in the fuel is the simplest application of additives. The analysis of additive and fuel blends aims to gain insight into how additives influence potassium release. The results are then used to estimate the effect of different amounts of additives. The goal is to evaluate for which biomass and in which type of combustion system the use of additive could be beneficial.
- The experimental results are linked to real applications via temperature. The alkali concentration in the flue gas is estimated with temperature profiles and typical operating conditions from different types of power plants. Moreover, the potential of reducing the alkali concentration in the flue gas by additives or changing the fuel is analyzed. By scaling the alkali release from the investigated biofuel types to the calorific value, a quantitative comparison and ranking of the fuels is possible. Additionally, the potential of additives to mitigate the potassium release in different combustion systems is evaluated. The overall objective is a practical assessment of which biomass type can be used in which combustion system and where the use of additives is promising to reduce ash-related problems.

4

Method

The focus of this work is the temperature-resolved analysis of the release of minor and trace elements from biomass, especially potassium. The experiments are conducted in an electrothermal vaporization unit (ETV) connected to an inductively coupled plasma optical emission spectrometer (ICP-OES). This method of analysis is described and validated in Paper I [23] and briefly explained in all other publications. However, the level of detail for describing an experimental setup in a journal article is limited.

This chapter gives a detailed overview of the ETV-ICP-OES system. While many parts have been published in Paper I, this chapter goes into more detail regarding best practices and limitations.

4.1 The ETV-ICP-OES System

The ETV-ICP-OES system combines two independent subsystems. The ETV is connected to the ICP-OES by a sample tube and a data link for the temperature signal. The ETV evaporates the sample at a controlled temperature and the ICP-OES determines the elemental concentration in the sample gas, providing quantitative and temperature resolved measurements of the elemental concentration in the sample. For successful measurements, the subsystems need to be carefully aligned. In this section, the ETV and the ICP-OES are presented individually, followed by a description of the interactions between the systems. Afterwards, the literature on ETV-ICP-OES systems is summarized.

ETV

The "ETV-4000d" is supplied by *Spectral Systems* (Fürstenfeldbruck, Germany). The system is equipped with an autosampler for the automated measurement of up to 50 samples and has an electrical power of 5 kW [174]. The core of the ETV is an electrically heated graphite furnace. The furnace can be rapidly heated to up to 3000 °C with heating rates up to $1000\,°\mathrm{C\,s^{-1}}$. The sample is inserted into the furnace in a graphite boat. An optical pyrometer in the furnace door reads the temperature of the sample boat for monitoring and control. Due to the high temperatures and the oxidizability of the material, all graphite parts need to be kept under an inert atmosphere when

the furnace is operated. The power electronics and the outer furnace rack are water-cooled.
Figure 4.1 shows a schematic setup of the ETV-ICP-OES system. There are three internal argon streams in the ETV and a reaction gas stream. The "Argon 2" stream is mixed with the modifier gas stream and injected into the furnace in the furnace door. This stream cools the optical pyrometer and avoids overheating. Carbon tetrafluoride (CF_4 or R14) is used as a modifier gas. The modifier gas is added to the furnace to avoid the formation of low-volatile compounds like carbides by promoting the formation of halides. Additionally, the modifier gas improves aerosol formation and enhances transport efficiency [175, 176]. However, there are no reports on the precise effect and exact reactions in the literature. The addition of the modifier gas results in clearer and smoother signals in the ICP-OES system. The flow rate of the CF_4 is low (2 mL/min) compared to the "Argon 2" stream (135 mL/min). The ETV atmosphere can be considered inert since the CF_4 concentration in the argon stream is less than 2 %, and the amount is small compared to the sample. The carrier gas, consisting of the "Argon 2" stream and the modifier gas, carries the evaporated sample out of the furnace.
"Argon 1" (420 mL/min) is introduced after the furnace to cool and dilute the sample gas [174]. This rapid and controlled cooling results in the condensation of the evaporated sample and the formation of a dry aerosol. This way, the sample does not condense on cooler parts of the tubing and is efficiently transported into the plasma. "Argon 3" purges the furnace shell and the graphite brackets that hold the furnace in place. The flow rate must be high enough to keep the graphite parts in an inert atmosphere during operation.

The internal pyrometer is adjusted by the manufacturer to the emission coefficient of graphite. Due to the aging of the quartz glass in the pyrometer optics, regular calibrations are necessary. The pyrometer is calibrated by keeping the furnace power constant and reading the boat's temperature with an external pyrometer through the opened furnace door. As an external pyrometer, a *Keller PKL 38 AF 1* (KELLER HCW GmbH, Germany) adapted by *Spectral systems*, is used. The operating range of the external pyrometer limits the calibrated temperature range of the ETV to between 500 °C and 2500 °C. While the calibration method is certainly not optimal, checks with an Infra-red camera show good agreement. The temperature is calibrated daily.

The ETV can be equipped with different graphite tube furnaces and sample boats. The manufacturer offers two sizes of tube furnaces (standard and maxi). The "Maxi-tubes" proved to be inadequate for temperature-resolved analysis due to condensation of the sample gas in the furnace. This was shown by heating the sample to a certain temperature, cooling the furnace, removing the sample boat, and then reheating the furnace. A clear signal could be observed once the initial temperature was exceeded. This clearly indicates condensation. Therefore, the ETV is operated with standard tubes in this work.
The sample boats can be purchased in "standard" and "premium" quality. The coating of the "premium" boats can be a challenge because of changing emission coefficients during the aging process. This can be overcome by only using boats of the same batch. However, the influence of the sample boat surface on the temperature signal is crucial. This limits the temperature accuracy of coatings as applied by Hommel et al. [177]. Uncoated "standard" boats were used in this work.
The graphite furnace tubes and sample boats are exposed to high temperatures, so they wear out over time and need to be changed. Difficulties with the temperature calibration can go back to a

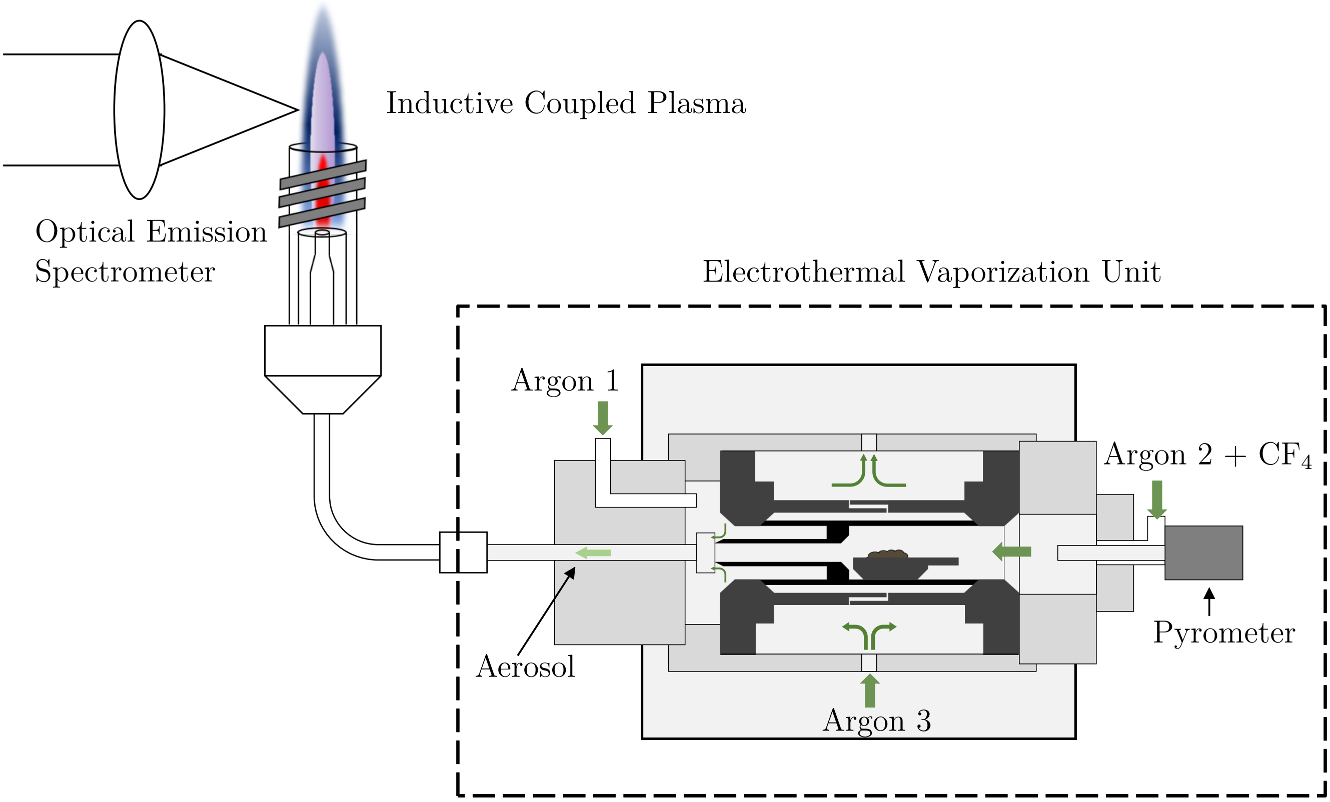


Figure 4.1: Setup of the ETV-ICP-OES System [23].

worn furnace tube. All gaskets are checked regularly, and the aerosol tube is cleaned every time the furnace is changed. The sample boats were changed once the autosampler had issues gripping them correctly.

ICP-OES

ICP-OES is a well-established method for the determination of minor elements in solid biofuels [104]. It is a standard procedure for the analysis of liquid samples. For the analysis of solid biofuels, the sample usually needs to be dissolved by microwave pressure digestion [178]. The general measurement method for the analysis of liquid samples and solid samples in the ETV is the same. The sample is introduced into the plasma, atomized, and ionized. When falling back from the excited state, each element emits specific radiation. An optical emission spectrometer analyzes these spectrums. By evaluating the intensity of certain wavelengths, the elemental concentration in the sample can be determined [179].

A *SPECTRO ARCOS FHM 22* (SPECTRO Analytical Instruments GmbH, Germany) ICP-OES system is used in all measurements [180]. For the monitoring of the device, a liquid control probe is analyzed on a daily basis("iCALisierung"). The system is operated in side-on mode, where the optics are placed perpendicular to the flow direction of the plasma. End-on operation, where the optic is placed at the top of the plasma, can increase the intensity of certain elements but requires careful and time-consuming calibration.

The used spectral lines for the analysis of samples in the ETV are highlighted in table 4.1. The interferences during ETV measurements are different from the liquid sampling methods. Therefore, each spectral line has to be selected individually. The ICP-OES software offers two regression methods to link the measured intensity to a concentration. The sensitive regression method has a linear correlation for low concentrations and a polynomial correlation of intensity and concentration for high concentrations. The system cannot analyze carbon due to the graphite parts in the ETV, and ICP-OES can not detect hydrogen, oxygen, fluorine, and inert gases [179].

Table 4.1: Wavelength used to detect the element investigated and the correlation coefficients of the calibration [24].

Element	Wavelength in nm	Regression method	Correlation coefficient
Ca	183.801	sensitive	0.9985
Cl	134.724	sensitive	>0.9999
K	769.896	sensitive	0.9999
Mg	202.647	linear	0.9998
Na	589.592	linear	0.9999
P	138.147	linear	0.9995
S	182.034	linear	0.9999

Method Development

The general challenge in method development is to get a signal in the ICP-OES that stands out clearly from the background noise but is not too intense to avoid overloading the optical chips. If the signal is too low, clear measurements are not possible. If the signal is too intense, the optical chips overload, and no calibration is possible. The chips can be overloaded if too much of a certain element or too much sample is introduced into the plasma. Multiple parameters affect signal intensity. In addition, the intensity bandwidth is element-specific, which complicates the development of multi-element methods. First, the different influencing factors and parameters are explained. Afterwards, the process of developing a method is described.

The most important factor is the sample. The mass, elemental concentration, and the chemically associated form determine the intensity of the ICP-OES signal. The sample mass is limited by the accuracy of the scale and the volume of the sample boat. Usually, between 2 mg and 5 mg of sample are placed in the sample boat.

The temperature profile determines how fast the sample is evaporated and introduced into the plasma. Higher heating rates increase the signal intensity. Very high heating rates reduce the accuracy of the temperature resolution. Low heating rates reduce the intensity and the signal-to-background ratio. This limits the accuracy of very slow heating programs. Holding the temperature constant for several seconds after devolatilization between 500 °C and 800 °C can avoid a general plasma overload. The heating rate is an easily adjustable parameter and should be addressed first if the signal intensity is too low or too high. In the measurements presented this work, the heating rate ranged from $20\,^{\circ}\mathrm{C\,s^{-1}}$to $40\,^{\circ}\mathrm{C\,s^{-1}}$.

The argon flows in the ETV and the plasma torch also influences the signal. These flows are recommended by the manufacturer of each system.

Another influencing factor is the injector diameter. The smaller the injector diameter, the faster the sample is injected into the plasma. This influences the height at which the sample is excited in the plasma and, thus, the intensity the optical emission spectrometer detects. The plasma torch also influences the intensity of the ICP-OES signal. Signal intensities are higher in end-on mode. All measurements in this work have been conducted in side-on mode because the signal intensities were satisfactory. Variations in the plasma torch setup are time-intensive and expensive.

The plasma power also has an effect on the intensity of the ICP-OES signal. However, the cooling gas streams need to be adjusted if the plasma power is changed. Therefore, a change in the plasma power should only be made by the manufacturer.

All of the above factors are hardware-related. The signal processing in the software is equally important. Each element emits radiation at multiple specific wavelengths. The intensity of these spectral lines varies. The selection of the line is based on the intensity and possible interference with other elements. While there are theoretically several possible spectral lines per element, usually, only one or two spectral lines can be used for analysis. The wavelength of the peak, the peak width, the background, and the area of interest of each line need to be defined. Moreover, the integration window needs to be adjusted to the temperature window in which the element is evaporated.

In liquid analysis, the entire spectrum of each measurement is recorded and integrated by the ICP-OES system. In ETV mode, the ICP-OES system records the spectral lines with 10 Hz. Since the data volumes would be too large, only the selected lines are recorded and not the entire spectrum. Therefore, the spectral lines need to be adjusted carefully because they cannot be changed in post-processing.

In the process of developing a method, first the expected elemental concentrations in the sample need to be assessed. Then, the elements of interest need to be defined. A ranking of the relevance can be helpful because the method design can change for the analysis of different elements. Afterward, the temperature profile and temperature range should be defined. The spectral lines can be selected based on previous ETV measurements or liquid ICP-OES methods. However, the suitability needs to be checked for every method.

The calibration of the elemental concentration starts with liquid single or multi-element standards. The use of liquid standards is more accurate because the dose can be adjusted better. In addition, these liquid standards are very homogeneous compared to solid reference materials. Once the liquid calibration is complete, solid matrix-matched certified reference materials need to be analyzed.

Before every measurement, a blank sample boat needs to be analyzed to determine the background and ensure that the system is clean. The correct operation of the ICP-OES and the calibration is checked with a sample of solid reference material. Additionally, the temperature calibration of the ETV is validated by pure silver and ammonium sulfate. After each batch measurement, the procedure of analyzing one sample boat of reference material, silver, and ammonium sulfate is repeated to ensure the correct measurement of all samples.

In summary, each method is always a compromise between the number of analyzed elements, the range of applicable samples, the accuracy of the elemental concentration, and the accuracy of the release temperature. The method developed in this work is focused on the temperature-resolved potassium release from various biofuels.

Literature on ETV-ICP-OES

Electrothermal vaporization as a method for sample introduction for inductively coupled plasma was first described by Nixon et al. in 1974 [181–183]. ETV can be used as a sample introduction for a variety of downstream analytical methods, the most prominent of which are ICP-OES and ICP-MS [182].
ETV in combination with ICP-OES is an established method of analysis for various samples [175, 176, 182–188]. However, the application is limited to certain niche analyses. Currently, there is only one type of commercial ETV setup available, which is also used in this work [174, 183].
Huang et al. identify various applications of ETV in their review, ranging from industrial to forensic and archaeological samples [183]. The fuel matrix and the elements of interest are critical to the analysis. Thus, only studies that analyze similar feedstocks are presented here. Of the wide range of samples analyzed in the literature, only a few groups have analyzed solid fuels or biomass samples.
De Gois et al. analyzed the chlorine and bromine content in coal [183, 189]. Vogt et al. investigated the inorganic compounds in coal, including the alkalis potassium and sodium [183, 187, 190]. Only few groups analyze potassium with an ETV setup. Mason measured the minor elements of solid plant materials by ETV and subsequent ICP-AES. He also tried to measure the potassium and calcium concentration but experienced issues with too high intensities [183, 191].
Detechva et al. conducted a study on the calibration possibilities for the analysis of minor and trace elements in plant materials. While they do not consider potassium, they highlight the impact of the modifier gas on the analysis of elements such as boron, titanium, and vanadium [176].
The most recent and related ETV analyses were conducted by Hommel et al. [175, 177, 192]. The group analyzed the K and S release from coal and plotted the signal intensity over the temperature. This simple form of temperature resolution and the addition of oxygen to the carrier gas stream stand out [177]. However, the oxidizing atmosphere requires a coating of the graphite parts, which limits the accuracy of the pyrometer. The switch in between oxidizing and inert atmosphere at 1500 °C is another challenge. In her dissertation, Hommel also investigated K and S release from four biomass and different sewage sludge samples [175]. While the measured overall concentrations show good agreement with other methods of analysis, there are no continuous temperature-resolved measurements of the release.

Overall, ETV-ICP-OES is used for elemental analysis in a wide range of applications and has proven to be a reliable analytical method. However, only few publications address solid biofuels or alkali release. Temperature-resolved quantitative analysis of potassium release has not been reported in the literature. Therefore, a new method for temperature-resolved analysis of potassium release needs to be developed and validated.

4.2 Validation of the ETV-ICP-OES

This section describes the validation of the ETV-ICP-OES system with a focus on electrothermal evaporation. The suitability of the method for the analysis of solid biomass is the primary goal of the validation.

The validation of the ETV-ICP-OES and the assessment of the accuracy of the chosen method can be divided into two steps. First, the regression of the calibration is analyzed. The calibrations with liquid standards, shown in table 4.1, and with matrix-matched reference materials, shown in table 2 of paper I, have correlation coefficients well above 99 % for all investigated elements. However, since this calibration is based on liquid standards or matrix-matched reference materials, a second validation step is necessary. The heterogeneity of the fuel and possible matrix effects require a comparison with different analytical methods. Since these methods are also subject to inaccuracies and the fuel samples investigated are heterogeneous, this comparison is of a qualitative nature. However, it ensures that there is no general offset in the ETV-ICP-OES analysis. The initial validation of the analysis of the concentration of seven minor elements in biomass by ETV-ICP-OES is performed by comparing the results with other analytical methods. This procedure is described in paper I [23]. The main results are summarized in this section. In addition, the validation of the more advanced liquid calibration method and the temperature validation are explained.

Figure 4.2 shows the comparison of different methods of analysis for the concentration of $\mathrm{K, Na, Ca, Mg, Zn, S}$, and P in five different biomass samples. The analytical methods include microwave pressure digestion in a HNO_3 or a HBF_4 solution, chemical fractionation (CF), ETV, and X-ray fluorescence analysis (XRF). The solutions of the HNO_3 and HBF_4 digestion, as well as the solutions of the CF processes, are analyzed in the ICP-OES. Figure 4.2 depicts the relative deviation of each analytical method from the HNO_3 measurements and the standard deviation. The HNO_3 measurements are chosen as a reference since this is the most established method of analysis [23, 104, 193].
The large deviations of the ETV sodium values from the HNO_3 measurements can be partly explained by the unusually high variation of all measurement methods, indicating a heterogeneous distribution of sodium between different batches of the same sample. In addition, low concentrations are very challenging for the ETV-ICP-OES system, as also shown by the zinc values. The suitability of the method should be evaluated for each sample. A detailed analysis of each element is presented in paper I. The results highlight that the ETV measurements agree well with the other analytical methods for the selected elements. The deviations are within the expected range for the analysis of heterogeneous biomass samples.

Potassium is the most important element regarding deposition and fine particle formation. The ETV analysis shows good agreement with the other methods for the potassium concentration in beech wood, as highlighted in Figure 4.3 [23]. Analyses of the solid residues from each leaching step of the chemical fractionation in the ETV demonstrate the accuracy and measurement range, and that all potassium is released in the ETV, regardless of the chemically associated form. A more detailed description of the conducted measurements is published in Paper I [23].

The method validated in Paper I is based on a calibration with matrix-matched certified reference materials. The measurements in Papers II-V are based on an improved calibration with liquid single or multi-element standards. This calibration method is more accurate because the homogeneous liquid standards can be pipetted more accurately than solid heterogeneous reference materials can be weighed. It also allows the measurement of matrix-matched certified reference materials to validate the calibration.

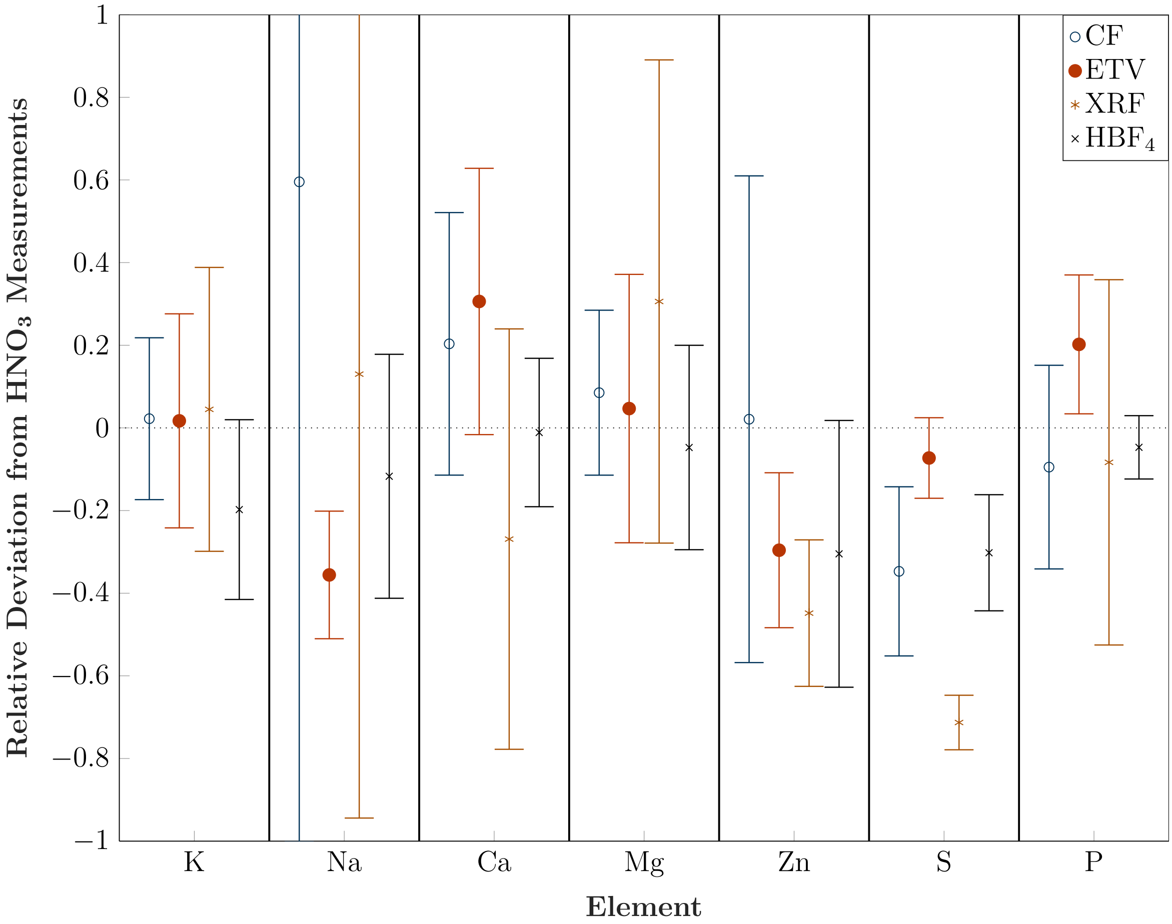


Figure 4.2: Relative derivation from HNO_3 measurements for the different methods of analysis sorted by element. [23].

"The internal pyrometer of the ETV is calibrated on a daily basis with an external pyrometer supplied by the manufacturer of the ETV system. To validate the calibration over a wide temperature range, two substances with distinct evaporation behaviors are analyzed. Ammonium sulfate decomposes at 280 °C into ammonia and sulfuric acid [194].This decomposition results in a clear and narrow peak in the sulfur signal of the ICP-OES. The analyzed ammonium sulfate was purchased from Carl Roth GmbH, Germany. To validate high temperatures, silver with a purity of 99.97 % obtained from LabNeed GmbH, Germany was evaporated in the ETV-ICP-OES. A clear silver signal was observed at the boiling point of 2212 °C [195]." [25]

With reproducible correlation factors above 99 % for the calibration with liquid standards and solid reference materials, the ETV-ICP-OES method has been proven reliable and accurate. Hence, the overall measurement deviations are significantly more affected by the heterogeneity of the samples by the precision of the method. [23, 25, 196].

"The reliability of the temperature control can be validated. While the measurements can be accurately reproduced, the validation shows a systematic offset, with the optical pyrometer reporting low temperatures too high. At high temperatures, the offset is smaller and the temperatures reported by the ETV have a tendency to be too low. This offset is due to the temperature range of the pyrometer used for calibration (500 °C-2500 °C). However, interpolation of the offset would

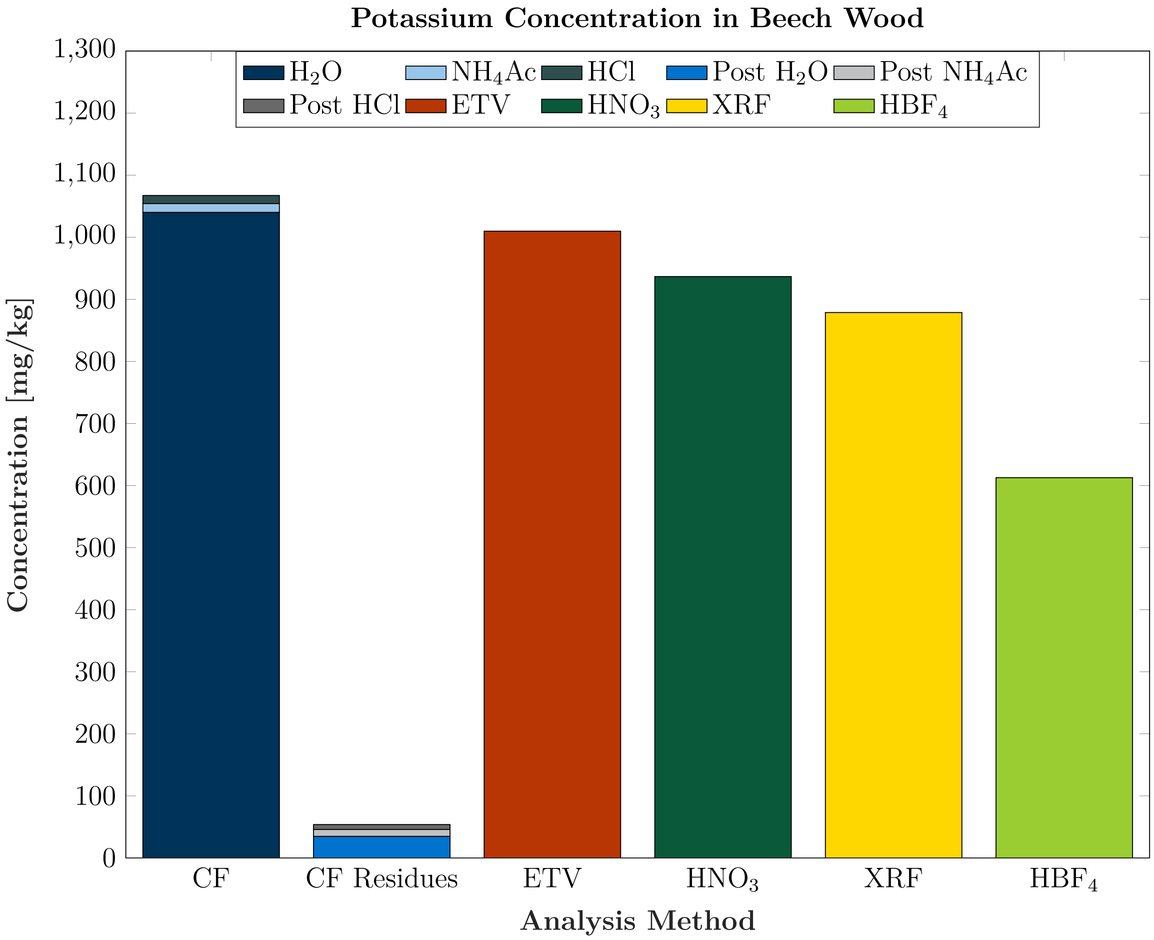


Figure 4.3: Potassium concentration in beechwood for different methods of analysis. “CF residues” shows the potassium concentration of the solid fraction after each CF step, analysed by ETV. [23]

hardly affect the temperature in the relevant temperature range, and the estimated offset is smaller than 100 °C. The temperature shown in the results is that measured by the ETV." [25]
Analysis of a boat of reference material, silver, and ammonium sulfate before and after each sample batch validates each measurement in the ETV-ICP-OES.

The literature review and comparison with other analytical methods show that ETV coupled with an ICP-OES is a reliable and accurate method for determining the elemental concentration of minor elements in biomass and for analyzing the temperature-resolved release behavior. However, the method must be carefully tuned for each sample type and element to obtain accurate and meaningful measurement results.

5

Summaries of Key Publications

This chapter summarizes the key publications. The goal is to show how the papers build on and relate to each other. The focus is on explaining how each paper fits into the larger picture. A detailed discussion of the results follows in chapter 6.

5.1 Validation of Electrothermal Vaporization for the Analysis of Biomass Samples and Comparison with Other Methods of Analysis

This section summarizes paper I. The full article is printed in appendix B.1
Reference: H. Mörtenkötter, D. Grünwald, S. Fendt, and H. Spliethoff: "Validation of Electrothermal Vaporization for the Analysis of Biomass Samples and Comparison with other Methods of Analysis", *Waste and Biomass Valorization*, Volume 14, pages 3489–3502, 2023,
https://doi.org/10.1007/s12649-023-02129-0

Summary: The first paper aims to evaluate the accuracy and reproducibility of biomass analysis by ETV-ICP-OES. The method is validated by comparing it to four other methods of analysis. A special focus lies on the chemically associated form of the alkalis and how this affects the quantitative analysis by ETV.
Figure 5.1 is the graphical abstract of the paper. Five different biomass samples, including wood, pretreated biomass, and stalk-like biomass, are analyzed. All samples are analyzed by CF analysis, which is a procedure to determine the water-soluble salts (e.g. $\mathrm{K}^+, \mathrm{Na}^+, \mathrm{Cl}^-$), organically associated ions (e.g. $\mathrm{Mg_2}^+, \mathrm{Ca_2}^+$), acid-soluble salts (e.g. Ca and Mg carbonates and sulfates) and inert minerals (e.g. silicates, oxides) by subsequent leaching of the sample in water (H_2O), 1 M ammonium acetate solution (NH_4Ac) and 1 M hydrochloric acid (HCl). Furthermore, microwave pressure digestions of all samples with HNO_3 and HBF_4 are prepared. The liquid CF and microwave pressure solutions are then analyzed by ICP-OES. Additionally, the ash composition of all samples is determined by XRF analysis.

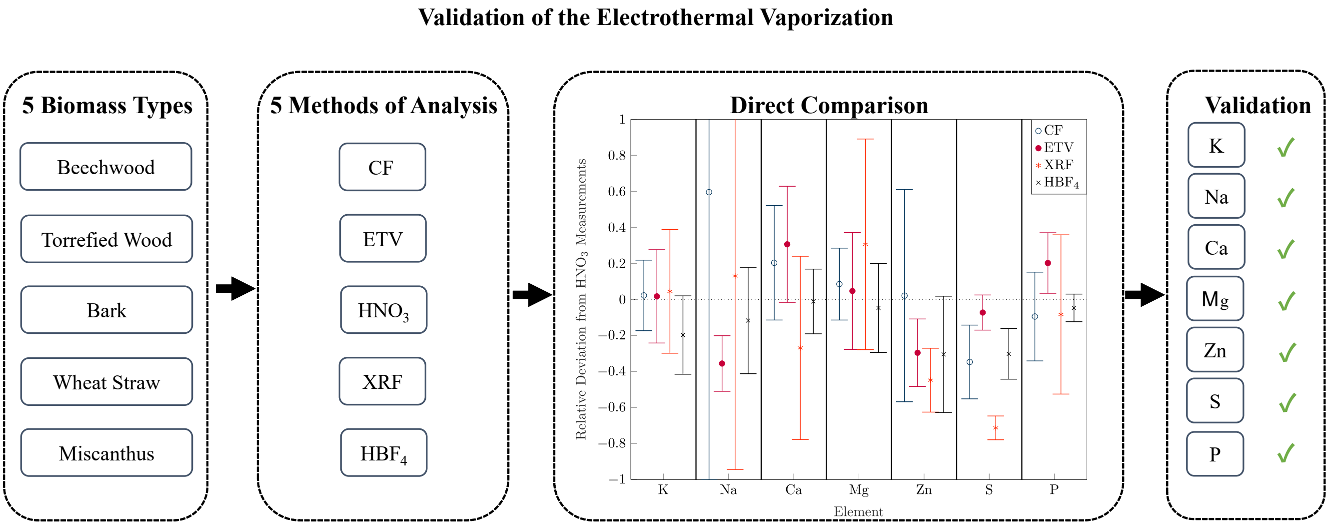


Figure 5.1: Graphical abstract of Paper I [23].

The ETV is calibrated using matrix-matched certified reference materials, with correlation coefficients exceeding 99 % ($R^2 > 0.99$) for all analyzed elements. All samples are heated up to 2400 °C. The comparison of the ETV results with the other methods of analysis highlights the reliability and accuracy of the ETV for the determination of the elemental concentrations of K, Na, Ca, Mg, Zn, S, and P. A direct comparison of the deviation of all measurements from the HNO_3 results is shown in the graphical abstract and figure 4.2. The deviation of the ETV-ICP-OES results from the microwave pressure digestion in HNO_3 are well within the expected range for the analysis of heterogeneous biomass samples. Furthermore, the deviations of the ETV system are smaller than the deviations of the other methods of analysis. The analysis of the CF residues in the ETV highlights that all alkali species are released in the ETV irrespective of the chemical association. Moreover, the developed method proved to be reliable for a wide range of different concentrations. Cl is not part of this comparison because the leaching solutions contain chlorine and XRF cannot determine the chlorine concentration with the chosen method.

All in all, this work proves that ETV-ICP-OES is an accurate method for the quantitative analysis of the concentration of minor elements in biomass. With the suitability of the method for the determination of the overall concentration established, the question of the accuracy of the temperature measurements, especially with regard to the particle size, arises. This question is answered in paper II.

Credit Author Statement

Hendrik Mörtenkötter: Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Dominik Grünwald**: Writing – review & editing, Investigation, Formal analysis, Data curation. **Sebastian Fendt**: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Hartmut Spliethoff**: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

5.2 Temperaturaufgelöste Freisetzung von Nebenelementen aus fester Biomasse

English: "Temperature resolved release of minor elements from solid biomass"
This section summarizes paper II. The full article is printed in appendix B.2. The paper was part of the conference proceedings of the "31. Deutscher Flammentag" and is the only German paper in this dissertation.
Reference: H. Mörtenkötter, C. Heilmeier, T. de Riese, S. Fendt, and H. Spliethoff, "Temperaturaufgelöste Freisetzung von Nebenelementen aus fester Biomasse", *31. Deutscher Flammentag*, 2023

Summary: This paper aims to validate the temperature measurements of the ETV and analyzes the influence of the particle size on the release behavior. The calibration method has been improved in this work compared to the first paper by using liquid single and multi-element standards. This method has the advantage that liquid standards are more homogeneous and can be dosed more accurately than solid reference materials. Matrix-matched certified reference materials are also used to control and validate each batch. Therefore, the validation of the previous paper is also valid for this method.
The temperature measurements of the internal pyrometer are checked by the analysis of substances with unimodal release characteristics. The ammonium sulfate decomposition at 280 °C and the silver boiling at 2212 °C validate the temperature signal.
In order to analyze the influence of the particle size, wood pellets are milled and then sieved into seven different size fractions. The fractions are then individually analyzed by ETV-ICP-OES. The temperature-resolved release rate of the different fractions is displayed in figure 5.2. The release rate from smaller particles is significantly higher than from larger particles but occurs in the same temperature range. Especially the smallest two fractions, <25 µm and 25 µm-100 µm, show much higher intensities for all seven investigated elements.
Microwave pressure digestions confirm the higher content of ash-forming elements in the smaller particles. This is consistent with the literature and likely goes back to the milling process in which the crystalline ash particles are easier milled than long-chained hydrocarbons. Therefore, the ash content in smaller particles is significantly higher. The release of K, Na, Cl, S, and P occurs in the same temperature window for all particle sizes, and these elements are fully released. Not all Ca and Mg are released from the smaller particles, as indicated by the ongoing release at 2400 °C. Nevertheless, the release of all elements occurs in overlapping temperature windows for all particle sizes, which demonstrates that the release is not limited by transport processes linked to particle size for the applied heating rates.

Overall, the temperature-resolved analysis of minor elements can be validated in terms of temperature accuracy and quantitative concentration determination. This is the basis for the deeper analysis of the temperature-resolved release patterns in the next paper.

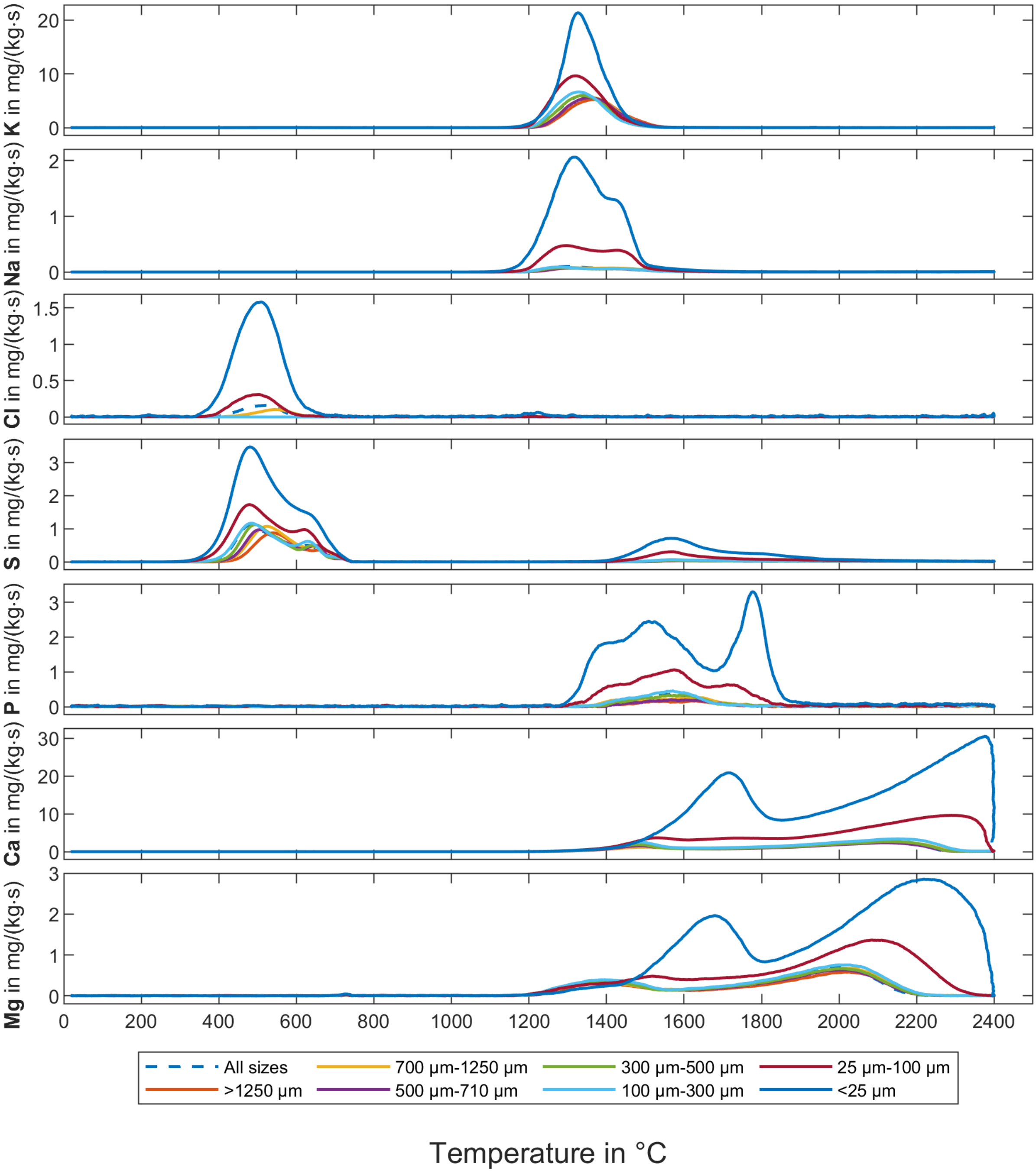


Figure 5.2: Temperature-resolved release of minor elements from wood pellets screened to different particle sizes [24].

Credit Author Statement

Hendrik Mörtenkötter: Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Carolin Heilmeier**: Writing – review & editing, Investigation, Formal analysis, Data curation. **Thorben de Riese**: Thorben de Riese: Writing – review & editing, Methodology, Conceptualization. **Sebastian Fendt**: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Hartmut Spliethoff**: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

5.3 Temperature resolved release of inorganic compounds from biomass

This section summarizes paper III. The full article is printed in appendix B.3
Reference: H. Mörtenkötter, C. Heilmeier, T. de Riese, S. Fendt, and H. Spliethoff: "Temperature resolved release of inorganic compounds from biomass", *Fuel*, Volume 357, 2024, https://doi.org/10.1016/j.fuel.2023.129939

Summary: In this paper, the temperature-resolved release of seven minor elements from ten different biomass samples is investigated. The samples include wood pellets, beech wood, torrefied wood, bark, damaged wood, miscanthus, silphie, sida, and wheat straw. For each sample, the release of K, Na, Cl, S, P, Ca, and Mg is simultaneously recorded. By analyzing multiple elements at once, this paper aims to investigate not only the elemental release but also the species that are released.
The potassium release from all investigated samples largely occurs between 1000 °C and 1500 °C. Compared to literature data, summarized in figure 2.2, the results show good agreement given that the experimental conditions, especially atmosphere and heating rate, differ significantly between the experiments reported in the literature. Chlorine and sulfur are released between 300 °C and 800 °C with a secondary release of sulfur above 1400 °C. Phosphorus release starts around 1400 °C and can continue to 2000 °C and more, depending on the biomass. There is a continuous release of calcium and magnesium at 2400 °C, indicating that not all compounds are released at this temperature. Overall, the temperature window in which elements are released differs significantly for different biomass types. K, Na, S, and Cl are completely released from all samples, while a continuous release of P, Ca, and Mg at 2400 °C can be observed from some samples.
Figure 5.3 shows the release patterns of miscanthus. The solid blue line shows the average over five measurements and the blue area highlights the standard deviation. The ETV-ICP-OES can only detect elemental concentrations, not molecules, but based on which elements are detected simultaneously, conclusions can be drawn about the molecular structure. Secondary gas phase reactions are suppressed by the rapid cooling and dilution in the ETV, therefore it is possible to observe only the released species. The analyses focus on a deeper understanding of the potassium release. The key finding of this work is the largely separate release of potassium and sodium on the one hand and chlorine and sulfur on the other. This stands in contrast to the assumption in the literature that potassium is largely released as KCl and K_2SO_4. Potassium is most likely primarily released as KOH or elemental potassium. These results may be explained by the suppression of secondary gas phase reactions in the ETV-ICP-OES system.While some potassium is released as KCl and K_2SO_4 in the ETV, the results highlight the release of KOH and elemental potassium. Thus, this work underscores the difference between released species and products of gas phase reactions.

In addition, the comparison of the different fuels highlights the impact of the fuel composition on the potassium release. The temperature range in which potassium is released can differ by up to 500 °C. The effect of the fuel composition on the potassium release and how additives can alter the release is discussed in detail in Paper IV.

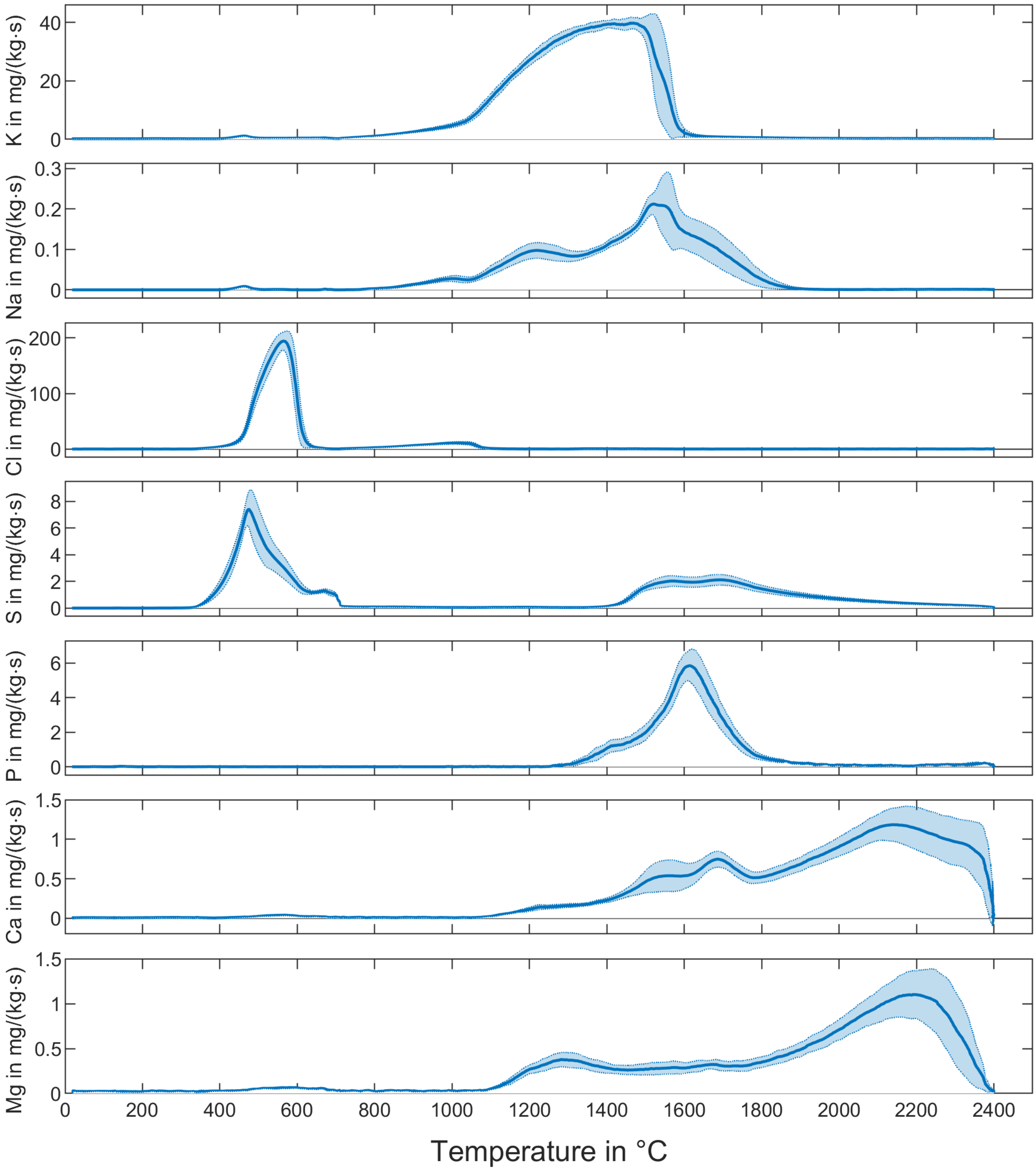


Figure 5.3: Release rate of minor elements from miscanthus averaged over five measurements. The light blue area highlights plus and minus one standard deviation [25].

Credit Author Statement

Hendrik Mörtenkötter: Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Carolin Heilmeier**: Writing – review & editing, Investigation, Formal analysis, Data curation. **Thorben de Riese**: Writing – review & editing, Methodology, Conceptualization. **Sebastian Fendt**: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.
Hartmut Spliethoff: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

5.4 Effects of Aluminosilicate Based Additives on Potassium Release and Ash Melting during Biomass Combustion

This section summarizes paper IV. The full article is printed in appendix B.4
Reference: H. Mörtenkötter, M. Kulkarni, L. Fuchs, F. Kerscher, S. Fendt, and H. Spliethoff, “Effects of aluminosilicate-based additives on potassium release and ash melting during biomass combustion,” *Fuel*, vol. 374, p. 132471, 2024. doi: https://doi.org/10.1016/j.fuel.2024.132471

Summary: Using the same ETV-ICP-OES method as in the previous article, this paper investigates the influence of additives on the potassium release and ash melting behavior. The goal is to evaluate the mixing of additives with the fuel, the simplest way of additive introduction. Moreover, the ability of different fuel indices to predict the potassium release and the influence of additives is analyzed. Miscanthus, torrefied wood, and beech wood are mixed with kaolin and CFA. The stoichiometric additive concentrations for each fuel and additive combination are calculated so that, theoretically, all fuel potassium could be bound in the aluminum-silicon systems of the additive. Afterwards, fuel samples are mixed with 100%, 200%, and 300% of the stoichiometric additive concentration. The temperature-resolved potassium release behavior is then analyzed by ETV-ICP-OES. In addition, ash samples of all blends and fuels are analyzed in an ash melting microscope.

In addition to laboratory results, the slagging and fouling tendencies of the fuels are evaluated with the most common fuel indices for biomass. The alkali index, the base-to-acid ratio, the Cl-ratio, and the S-ratio are calculated for each fuel and additive mixture based on XRF analyses. The indices rank the fuels in different order and come to drastically varying conclusions regarding the expected impacts on the power plant operation. Moreover, the alkali index even predicts a negative impact of additives in the fuel on the slagging and fouling probability. Since slagging and fouling are strongly linked to potassium compounds in the gas phase, the fuel indices should also correlate with the potassium release. However, comparing the measured potassium release with the fuel indices shows little to no agreement. Therefore, the fuel indices studied are unsuitable for comparing biofuels as different as those investigated in this work.

The additives have a different effect on the investigated fuels, both regarding the ash-melting and the potassium release behavior. No positive effects could be observed for mixing kaolin or CFA with beechwood. Additives can increase ash stability or postpone the potassium release by binding the potassium in more temperature-stable compounds such as ilite, kalsilite, or leucite. The potassium in beechwood is likely already bound in temperature-stable compounds.

The temperature-resolved potassium release intensity and the ash shrinkage of miscanthus mixed with different concentrations of CFA are shown in figure 5.4. The potassium release is clearly shifted towards higher temperatures for increasing CFA concentrations. The secondary potassium release peak for 200 % and 300 % CFA at approx. 1500 °C indicates the release of potassium compounds that were included in the additive. The ash melting properties of miscanthus are significantly improved by the additive. Pure miscanthus ash starts to inflate to more than two times the initial volume before rapidly collapsing at roughly 1000 °C. This inflation can be explained by a partially molten surface that traps volatile species. The release from the same batch of miscanthus is shown in Figure 5.3, indicating that the entrapped volatile species are rich in chlorine and sulfur. Additives can postpone the ash melting by more than 300 °C. Similar effects are observed for kaolin. The additives also postpone potassium release and ash melting of torrefied wood, but the positive effects are smaller. All in all, this paper highlights the importance of temperature-resolved potassium release analysis because no reliable method exists to predict the slagging and fouling behavior of a biofuel based only on the composition. Moreover, the effect of additives is highly fuel-specific and also difficult to predict.

While these laboratory results provide useful insight into fuel and additive behavior, many other factors must be taken into account for a meaningful application of these data to real combustion processes. This transfer of laboratory data to existing power plants is the focus of the final paper of this dissertation.

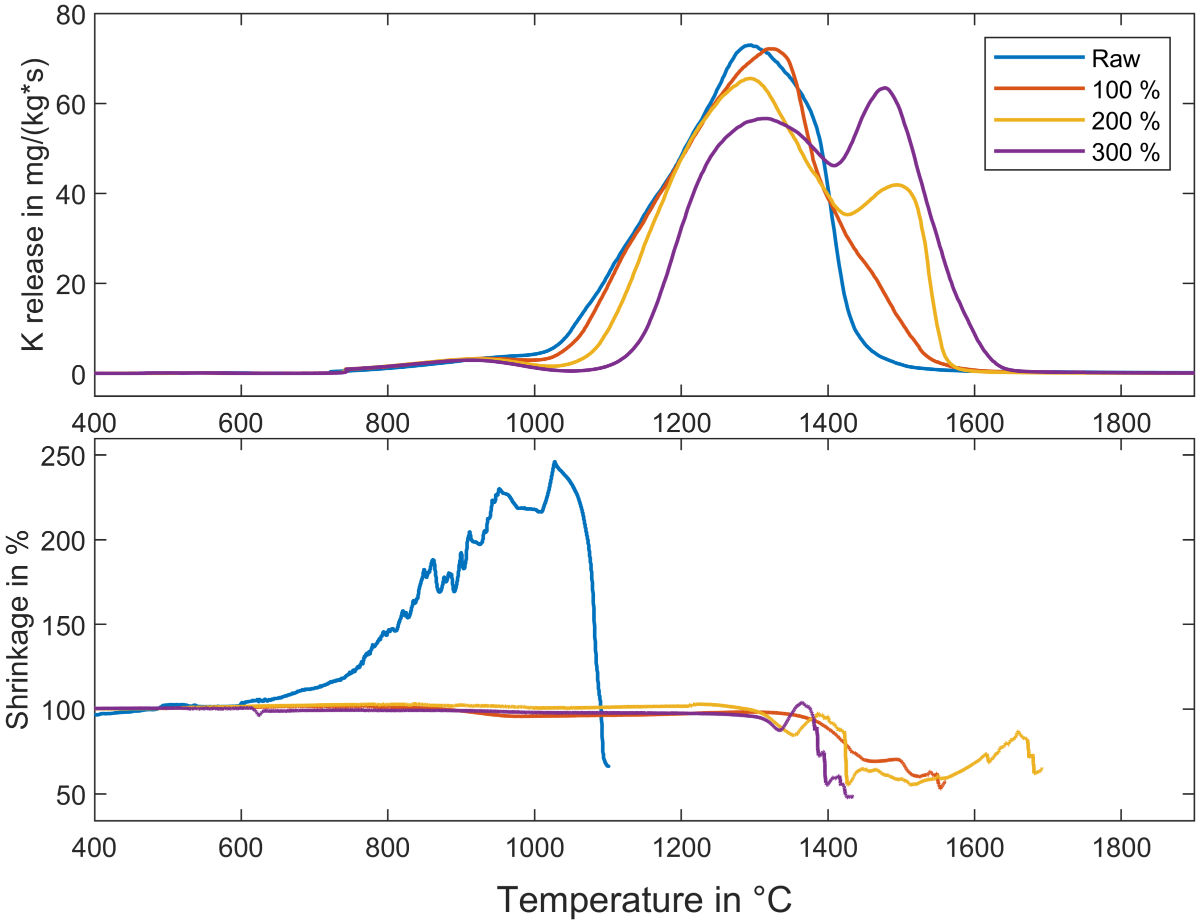


Figure 5.4: Potassium release and ash melting behavior of miscanthus for different concentrations of CFA. 100 % CFA equals 4.22 wt.% [26].

Credit Author Statement

Hendrik Mörtenkötter: Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Manas Kulkarni**: Investigation, Formal analysis, Data curation. **Lennart Fuchs**: Investigation, Formal analysis, Data curation. **Florian Kerscher**: Writing – review & editing, Methodology, Conceptualization, Funding acquisition. **Sebastian Fendt**: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Hartmut Spliethoff**: Writing – review & editing, Supervision, Project administration, Funding acquisition.

5.5 Potassium Release and Mitigation by Additives in Different Biomass Combustion Systems

This section summarizes paper V. The full article is printed in appendix B.5
Reference: H. Mörtenkötter, F. Kerscher, M. Schönsteiner, S. DeYoung, S. Fendt, and H. Spliethoff: "Potassium release and mitigation by additives in different biomass combustion systems," *Fuel*, Volume 369, p. 131800, 2024, https://doi.org/10.1016/j.fuel.2024.131800

Summary: This paper builds on all previous publications and combines the laboratory results. The objective of this paper is to assess the expected deposition formation for each fuel. Deposition formation is extremely complex and requires consideration of the atmosphere, flue gas temperature, wall temperature, and flow conditions. However, the most relevant condition for deposition formation during the combustion of solid biomass is the amount of potassium in the gas phase.

The temperature-resolved potassium release of ten biofuels is scaled to the calorific value and then compared to typical temperature profiles of commercial combustion systems. In addition, mixtures of kaolin and CFA with beechwood, torrefied wood, and miscanthus are investigated. The maximum combustion temperature relevant for the potassium release is analyzed for fluidized bed, grate, and suspension firing systems. Afterwards, the temperature profile of the fluidized bed system in Altenstadt (Germany), a MARTIN grate system (MARTIN GmbH für Umwelt- und Energietechnik, Gemerany), and the pulverized fuel system of Avedøre unit 2 (Denmark) are analyzed in detail.

The laboratory experiments differ from the conditions in power plants especially regarding heating rate, particle size, residence time, and atmosphere. These conditions also vary between the different power plant types and can impact the potassium release. The heating rate in the ETV experiments is similar to that in grate firing systems. Particle size and residence time are similar to the conditions in fluidized bed combustion system. The most important difference between the ETV experiments and the combustion applications is the inert atmosphere in the ETV. This needs to be considered when evaluating the results.

Figure 5.5 shows the cumulative potassium release from the investigated biofuels over the temperature. The temperature window for fluidized bed, grate, and suspension fired systems are highlighted. In addition, the release relevant temperature for the three individually analyzed power plants is marked with a vertical line. At the typical temperatures in fluidized bed systems, little to no potassium is released into the gas phase. Most of the potassium is released in the temperature range of grate firing systems. At the temperatures in pulverized fuel systems, almost all potassium is released into the gas phase.

In fluidized bed systems, additives could be used to prevent bed agglomeration. Since little potassium is released to the gas phase, the release-inhibiting effect of additives is hardly relevant. In grate systems, the operating conditions and additives could have significant impact on the amount of potassium released to the gas phase. The ability of additives to postpone the potassium release is particularly relevant at temperatures between 1000 °C and 1400 °C, the operating range of grate systems. Reducing the temperature on the grate by air-staging or other measures could also significantly reduce the potassium concentration in the gas phase.

The temperature in suspension systems is so high that almost all potassium is released. Additives could be used to capture potassium compounds in the gas phase once the flue gas is cooled but

not to inhibit the initial release of the potassium.
The ranking of the cumulative potassium release from the different fuels enables a rating of the investigated fuels and a pre-selection for a certain combustion system. Based on the comparison with wood pellets, damaged wood could potentially be burned in suspension-fired power plants.

Overall, this paper relates the temperature-resolved laboratory potassium release data to power plant applications. The limitations of transferring laboratory results to combustion applications are critically discussed, and the insights into the expected potassium release in different types of power plants, as well as the impact of additives, are highlighted.

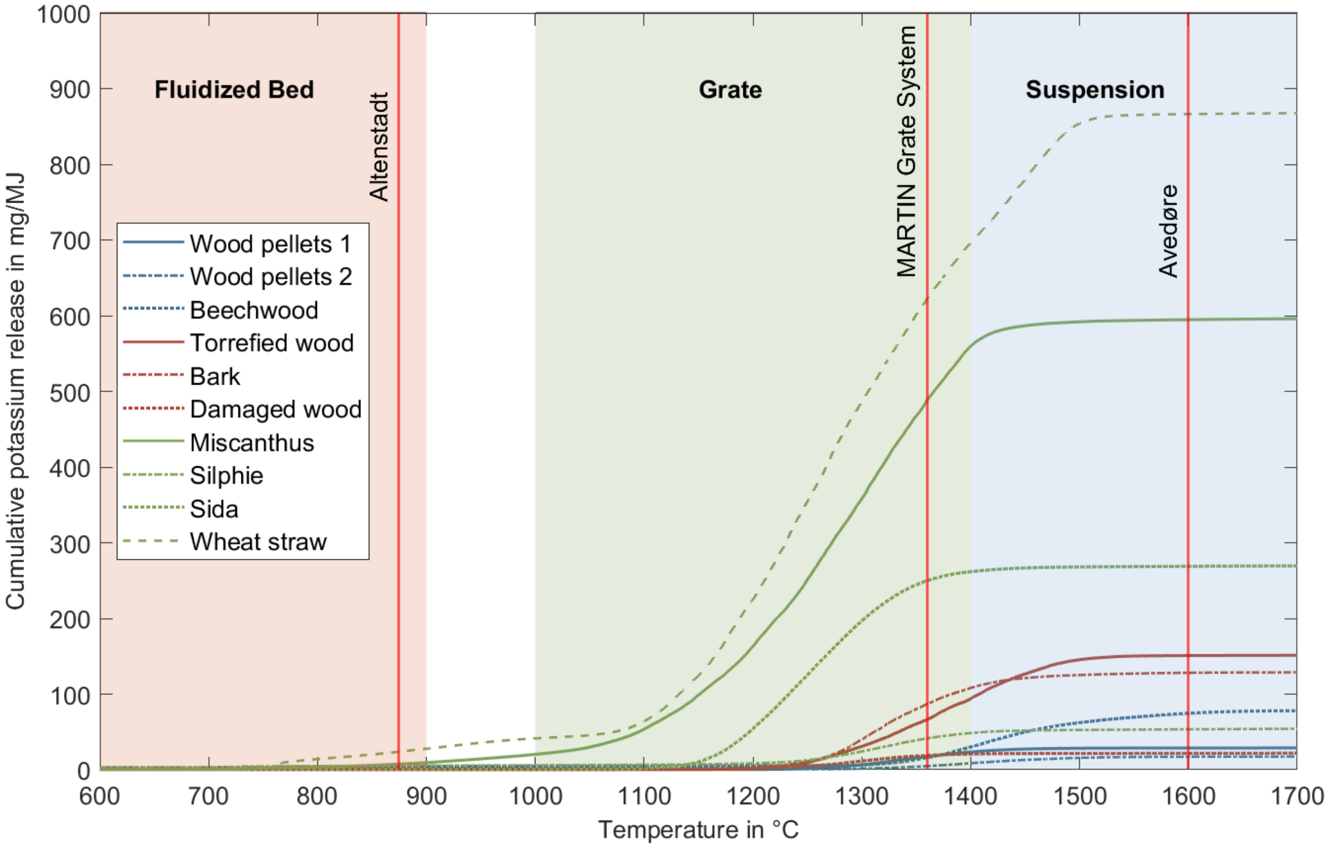


Figure 5.5: Temperature-resolved potassium release from different biofuels. The typical temperature range of different power plant types is highlighted [27].

Credit Author Statement

Hendrik Mörtenkötter: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration. Writing – original draft.
Florian Kerscher: Conceptualization, Funding acquisition, Writing – review & editing. **Max Schönsteiner**: Data curation, Resources. **Stefan DeYoung**: Data curation, Resources, Writing – review & editing. **Sebatian Fendt**: Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Hartmut Spliethoff**: Conceptualization, Funding acquisition, Project administration, Supervision.

6

Discussion and Conclusion

This chapter summarizes and discusses the main results of this work. First, the capabilities and limitations of the experimental method are outlined. The challenges of transferring the laboratory data to full-scale combustion applications are critically evaluated before the key findings of this work are highlighted as a basis for recommendations for future research.

Analytical Method

The ETV-ICP-OES method for the analysis of solid biomass samples proved to be reliable and reproducible. The system can be consistently calibrated with correlation coefficients exceeding 99 % ($R^2 > 0.99$) for all analyzed elements. Comparison with other analytical methods shows that the accuracy of ETV-ICP-OES is well within the requirements of fuel analysis. The deviation of the ETV-ICP-OES results is small compared to other analytical methods and likely dominated by the heterogeneity of the analyzed samples. The concentrations of $\mathrm{K, Na, Cl, S, P, Ca,}$ and Mg can be reliably determined with a high reproducibility. [23]

Accurate temperature measurements of the sample over the entire temperature range are challenging because the graphite tube furnace is resistively heated, and the sample is constantly changing. Validation of the internal pyrometer by analysis of ammonium sulfate and silver shows that the temperature accuracy is within 100 °C. In addition, the temperature measurement is found to be consistent and reliable, allowing different ETV measurements to be compared with high confidence. Since the heating rate limits the temperature accuracy of the measurements and directly influences the intensity of the ICP-OES measurements, the validation is limited to the investigated heating rates. [24]

Ultimately, the accuracy of the method can only be estimated. The comparison with literature data shows good agreement, so the different measurement conditions in comparison with combustion systems are probably more decisive than the accuracy of the system itself. Overall, an accurate method for quantitative and temperature-resolved analysis of minor element release from solid biomass in the ETV-ICP-OES system has been developed and validated for the entire temperature range of thermochemical conversion processes.[23, 24]

Potassium Release

The focus of this work is the analysis of the potassium release behavior. The potassium release of ten different biomass samples is continuously measured until all potassium is released.

Most of the potassium is released between 1000 °C and 1500 °C, but there are significant differences between the various biomass types. The potassium release data shows good agreement with the literature, even though some groups report the onset of the release at lower temperatures. This earlier onset could be explained by oxidation processes or longer residence times in these experiments. [25]

The comparison of different biomass types highlights the differences in the release behavior. The onset of the release varies by up to 500 °C between stalk-like biomass and woody biofuels. The amount of potassium released ranges from 20 mg/MJ for wood pellets to 800 mg/MJ for wheat straw. Moreover, the comparison can be used for fuel selection. Due to the similar release behavior, damaged wood can probably be used in the same combustion systems as wood pellets in terms of slagging and fouling behavior [27].

The release patterns of the ETV indicate that potassium is released predominately as KOH or elemental potassium because chlorine and sulfur are largely detected at different temperatures than potassium. In literature, multiple release pathways are postulated but rarely quantified. The low release of KCl and K_2SO_4, which are the predominant species in combustion systems, highlights the significance of secondary gas phase reactions. A distinction between species that are released from the fuel and formed in the gas phase is difficult in many experimental setups. In the ETV, most gas phase reactions are suppressed by dilution, rapid cooling, and continuous sample gas extraction. The ETV results indicate that KCl and K_2SO_4 in the flue gas of a combustion process are probably, to a large extent, products of gas-phase reactions since the potassium is released primarily as KOH or elemental potassium. The suppression of gas phase reactions in the ETV allows a clearer and more independent analysis of the release but also results in the persistence of species that are likely to react in the gas phase of combustion processes. These characteristics of the ETV-ICP-OES must be considered when evaluating the experimental results. [25]

Overall, the simultaneous, temperature-resolved analysis of multiple elements allows an evaluation of the released species. The continuous measurement of potassium release over the entire relevant temperature range permits a more detailed analysis of the release behavior compared to literature data.

Influence of Additives

The ETV results highlight that there is a temperature window in which kaolin and CFA can significantly reduce the amount of potassium released into the gas phase from miscanthus and torrefied wood. However, this potassium retention could not be observed in beech wood. The comparison of the ash melting microscope and the ETV-ICP-OES results highlights the correlation between ash melting and potassium release. Additives can bind highly volatile potassium compounds with low melting temperatures and thereby simultaneously decrease the potassium release and increase the ash stability. However, the effect of the additive is highly fuel-specific, and the evaluated fuel indices are neither able to predict the influence of the additive nor suitable for comparing a wide range of biofuels. [26]

For the practical application of additives, it must be considered that this potassium capture is highly fuel-specific and only relevant in a relatively small temperature range. The stoichiometric amount of kaolin and CFA significantly increases the ash melting temperature of miscanthus and torrefied wood, and further increases in additive concentrations do not increase the ash melting temperature much more. The potassium release from these fuels can be shifted almost continuously with increasing amounts of additives.

While the retention effect of additives could be proven in the ETV-ICP-OES, it can not be differentiated whether the potassium is released and then captured by the additive or if the reactions occur in the solid phase. Moreover, due to the constant extraction of the sample gas, the interaction of potassium species in the gas phase and the additive cannot be measured. Therefore, no positive effect of CFA in beechwood could be observed in the ETV even though Nowak Delgado et al. found a significant reduction of fine particle emissions for the same fuel and additive in pulverized fuel combustion systems [18]. The variation in the results indicates that the potassium is included in the additive during the cooling phase but not retained in the additive throughout the entire combustion process [26]. Ultimately, the combustion system must be considered when evaluating the use of additives.

Link to Combustion Processes

The central question of this work is how the experimental results can be transferred to combustion applications and which conclusions can be drawn. A careful discussion of the limitations is necessary before presenting the main findings.

The experiments in the ETV-ICP-OES system differ from commercial-scale combustion systems regarding heating rate, particle size, flow conditions, and atmosphere. These conditions also vary significantly between different types of combustion systems and depend on the operating conditions. No operating parameter value can be singled out to represent a type of combustion system. As a result, the comparison of the ETV experiments with different types of combustion systems is limited to a qualitative comparison. For a quantitative comparison, an exact operating point would be required. The heating rate of $20\,^{\circ}\,\mathrm{s}^{-1}$ in the ETV experiments is similar to that of fluidized bed systems, faster than in grate systems but much slower than in suspension systems [27]. Lower heating rates may result in higher cumulative release due to longer residence times. Very high heating rates result in such rapid release of the volatiles that inclusion reactions in ash components are inhibited, which can also increase the cumulative potassium release for a given temperature [25, 94]. Due to this partially contradicting effect of the heating rate, the effect of the difference between the ETV experiments and suspension combustion systems is difficult to assess. However, a comparison of the release of heavy metals in the ETV-ICP-OES with the release in a wire mesh reactor and an entrained flow reactor under gasification conditions demonstrate good agreement [197]. The heating rate in fluidized bed and grate systems is in the same order of magnitude as in the ETV experiments, so the difference in heating rate is likely neglectable for the transfer to fluidized bed and grate systems. [27]

The analysis of different particle sizes in the ETV, ranging from smaller than 25 µm to larger than 1 mm, showed that the release temperature is not affected by the particle size for the given heating rates. Therefore, it can be assumed that the influence of the particle size is relatively small. [24]

The flow conditions in the ETV are comparable to grate systems but differ significantly from

pulverized fuel combustion. The sample gas is continuously extracted in the ETV so the char or ash can not react with the gas phase. This needs to be considered when comparing the results to systems in which the char and ash are entrained in the flue gas.
The atmosphere is the most important difference between the ETV experiments and combustion applications. The ETV operates under an argon atmosphere to prevent oxidation of the graphite components, while the release in power plants happens under oxidizing conditions. Oxidation processes generally enhance the release by increasing the temperature. Moreover, oxygen can react with solid potassium compounds in the fuel, which might result in the release of different potassium species. These two influencing mechanisms are difficult to differentiate in experimental setups because the local temperature in a combustion process is hard to measure, and the potassium release involves multiple different species [89]. For an accurate analysis, the local atmosphere surrounding the fuel particle would need to be considered, which varies drastically between different combustion systems. Since the potassium release data from ETV-ICP-OES show good agreement with literature data measured under oxidizing conditions, the error from measuring release in an inert atmosphere appears to be acceptably low for a broad transfer of release data to different types of combustion systems. Moreover, Hommel et al. investigated the influence of the atmosphere on the potassium release from coal in an ETV system up to 1500 °C and highlight that the influence of the atmosphere is fuel-specific. The partially contradictory results suggest that oxygen can promote and postpone the potassium release, depending on the chemically associated form [27, 177].
The overall influence of the atmosphere is difficult to assess, but there is no indication that potassium release in oxidizing conditions is significantly different from inert atmospheres. Ultimately, the comparison and ranking of similar fuels is possible irrespective of the atmosphere.

The temperature range relevant for the potassium release is between 1000 °C and 1400 °C, which is above the typical combustion temperatures of fluidized bed systems, indicating that hardly any potassium is released to the gas phase in these systems. Additives can improve ash stability but are not relevant for the suppression of potassium release in fluidized bed systems.
Almost all potassium, even potassium bound in additives, is released to the gas phase at typical suspension firing temperatures. Therefore, additives can only bind potassium species during cooling and effectively reduce the gas phase concentration of problematic species.
Most potassium is released at typical grate firing temperatures. Since the release occurs in a temperature window of roughly 300 °C, a shift of the release temperatures by additives could significantly reduce the amount of potassium that enters the gas phase. A reduction of the temperature on the grate could also have a significant impact on the potassium release. [27]

Mixing additives with the fuel is effective in suppressing the potassium release at grate combustion temperatures but redundant at the temperatures in suspension firing or fluidized bed systems. In fluidized bed systems, additives could be easily mixed with the bed material, but the overall potassium release is very low. In grate systems, mixing the additive with the fuel can be difficult for the bulky fuels typically burned in grate systems. Additives can be added to the fuel in a pretreatment process such as pelleting. However, a separate injection of the additive into the combustion chamber might be easier and cheaper to implement. In suspension firing systems, additives can be mixed with the fuel during the milling process or could be blown in with the primary or secondary air. Additives mixed with the fuel can capture the problematic species during the cooling process, but the surface area degradation of the additive due to exposure to high temperatures can reduce the inclusion efficiency. This degradation is additive-specific and needs to be considered when implementing an additive introduction system [19]. The optimum quantity and type of additive introduction must, therefore, be assessed individually for each combustion system, each fuel, and each additive.

Overall, the experimental results and transfer to different power plants highlight the varying potassium release behavior of different biofuels and the potential of additives to postpone potassium release in certain combustion applications.

Recommendation for Future Work

In future studies, the number of elements analyzed in the ETV-ICP-OES should be extended. For accurate analysis, the ICP-OES intensities need to be sufficiently high. Therefore, the method is suited for the analysis of minor and trace elements with sufficiently high concentrations.

Analysis of more elements could improve the understanding of ash behavior, especially at high temperatures. Heavy metal analysis could provide insights into their fate during thermochemical conversion processes. This may help to evaluate ash utilization options. In addition, temperature-resolved analysis by ETV-ICP-OES could be used to develop phosphorus recycling strategies by identifying the influence of fuel composition and additives on the phosphorus release.

The influence of the atmosphere on the elemental release should be investigated in more detail. A comparison with other reactors and experimental setups could offer valuable insights.
This work has a strong focus on biomass combustion and potassium release. The experimental results could also be applied to pyrolysis or gasification processes.

The relevant temperature range in which additives alter the potassium release should be investigated in more detail. In addition, the effect of additive concentration should be further investigated. More additives and the potential of blending different biofuels should be investigated. The experimental results highlight the potential for reducing the temperature in grate systems to drastically decrease the potassium release. These findings should be verified in pilot-scale grate combustion systems and potentially be applied in full-scale grate combustion systems.

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A

Appendix

Abbreviations

BFB bubbling fluidized bed

CF chemical fractionation

CFA coal fly ash

CFB circulating fluidized bed

CFD computational fluid dynamics

ETV electrothermal vaporization

ICP-AES inductive coupled plasma-atomic emission spectroscopy

ICP-MS inductively coupled plasma mass spectrometer

ICP-OES inductively coupled plasma optical emission spectrometer

IGCC integrated gasification combined cycle

IPCC Intergovernmental Panel on Climate Change

KEMS Knudsen effusion mass spectrometry

LHV lower heating value

LIBS laser-induced breakdown spectroscopy

MBMS molecular beam mass spectrometer

MSW municipal solid waste

PM particulate matter

TGA thermogravimetric analysis

XRF X-ray fluorescence analysis

Declaration of Generative AI

During the preparation of this work the author used *DeepL* (DeepL SE, Germany) and *Grammarly* (Grammarly Inc., USA) to improve wording, grammar and punctuation. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

B Included Publications

B.1 Validation of Electrothermal Vaporization for the Analysis of Biomass Samples and Comparison with other Methods of Analysis

Reference: H. Mörtenkötter, D. Grünwald, S. Fendt, and H. Spliethoff: "Validation of Electrothermal Vaporization for the Analysis of Biomass Samples and Comparison with other Methods of Analysis", *Waste and Biomass Valorization*, Volume 14, pages 3489–3502, 2023, https://doi.org/10.1007/s12649-023-02129-0

B.2 Temperaturaufgelöste Freisetzung von Nebenelementen aus fester Biomasse

Reference: H. Mörtenkötter, C. Heilmeier, T. de Riese, S. Fendt, and H. Spliethoff, "Temperaturaufgelöste Freisetzung von Nebenelementen aus fester Biomasse", *31. Deutscher Flammentag*, 2023

B.3 Temperature resolved release of inorganic compounds from biomass

Reference: H. Mörtenkötter, C. Heilmeier, T. de Riese, S. Fendt, and H. Spliethoff: "Temperature resolved release of inorganic compounds from biomass", *Fuel*, Volume 357, 2024, https://doi.org/10.1016/j.fuel.2023.129939

B.4 Effects of aluminosilicate-based additives on potassium release and ash melting during biomass combustion

Reference: H. Mörtenkötter, M. Kulkarni, L. Fuchs, F. Kerscher, S. Fendt, and H. Spliethoff, “Effects of aluminosilicate-based additives on potassium release and ash melting during biomass combustion”, *Fuel*, vol. 374, p. 132471, 2024. doi: https://doi.org/10.1016/j.fuel.2024.132471

B.5 Potassium release and mitigation by additives in different biomass combustion systems

Reference: H. Mörtenkötter, F. Kerscher, M. Schönsteiner, S. DeYoung, S. Fendt, and H. Spliethoff: “Potassium release and mitigation by additives in different biomass combustion systems”, *Fuel*, Volume 369, p. 131800, 2024, https://doi.org/10.1016/j.fuel.2024.131800