Phosphorus recovery from sewage sludge fluidized bed gasification processes

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Abstract

One of the most sustainable pathways of sewage sludge treatment in recent years has been thermal conversion. The benefits of thermal treatment of sewage sludge are the recovery of energy or valuable chemical products, the destruction of harmful organic compounds, the separation of heavy metals from the P-rich coarse ash fraction, and the decreased and sanitized ash volume. The ashes created by these thermal conversion processes of sewage sludge are often rich in P that is mostly present in minerals with low plant-availability such as apatite. Due to the enrichment of P in the created ashes, a variety of post-processing steps have been developed to recover P from sewage sludge ashes. One proven way for the sustainable recovery of P from such ashes is thermal post-processing with alkaline salts, e.g., Na_2SO_4 or K_2CO_3, which was able to transform less plant-available phosphates in the sewage sludge into more plant-available alkali-bearing phosphates. Based on these results, one could facilitate creating these phosphates with enhanced plant-availability by providing the chemical potential to form them already during the thermal conversion process of sewage sludge.

This thesis aims to increase the current knowledge about the ash transformation processes of P and to suggest suitable process parameters for the alteration of the phosphate speciation in sewage sludge ashes by co-conversion with alkaline-rich agricultural residues. More specifically, the possibility of incorporating K derived from agricultural residues in phosphate structures derived from sewage sludge was evaluated with respect to the influence of the process temperature, the conversion atmosphere, and the fuel mixture. The studied parameters were chosen to generate knowledge relevant for fluidized bed gasification processes, with a special focus on dual fluidized bed (DFB) gasification systems.

The applicability of feldspar bed materials in fluidized bed gasification systems was investigated to enable the substitution of the commonly used olivine, which often contains heavy metals (potentially contaminating recovered ashes), and quartz, which is very reactive towards fuel-derived K and potentially leads to bed material fragmentation and bed agglomeration (Paper I & II). Subsequently, the thermodynamic potential for the alteration of the P-species in sewage sludge ash during co-combustion and co-gasification processes with agricultural residues was investigated (Paper III). Thereafter, an experimental evaluation of the ash transformation chemistry in thermal conversion processes of sewage sludge with

different types of alkali-rich agricultural residues in temperatures relevant for fluidized bed technology was conducted (Paper IV & V).

The methodology employed was chosen with respect to the state of technology of the specific investigated process. Paper I & II applied SEM, EDS, XRD, and thermodynamic equilibrium modeling for bed material samples derived from an industrial indirect gasifier. Paper III applied thermodynamic equilibrium calculations to theoretically evaluate ash compositions resulting from co-conversion of sewage sludge and agricultural residues. Paper IV & V employed SEM, EDS, ICP-AES/MS, XRD, and thermochemical modeling on ash samples derived from single pellet lab-scale experiments.

The results obtained by analysis of bed material from indirect wood gasification showed the difference in interaction mechanism for K-feldspar and Na-feldspar, most notably the enhanced disintegration of Na-feldspar by K originating from the fuel (Paper I & II). Thermodynamic models employed for fuel mixtures of sewage sludge and agricultural residues showed the thermodynamic preference for the formation of the desired alkali-bearing phosphates (Paper III). Experiments conducted with these fuel mixtures (Paper IV & V) supported the theoretical findings, and the influence of temperature and process conditions could be obtained. However, practical investigations also showed that attainment of the desired ash composition is subject to significant restrictions.

Derived from the elaborated results and discussions, it was possible to assess the critical process and fuel parameters for the development of up-scaled gasification processes focusing on the conversion of sewage sludge with the aim of creating improved phosphate formation in the ash. The selection of a suitable bed material in fluidized bed conversion and the transformation mechanisms defining the ash chemistry were found to be of vital importance for future applications. The pursuit of the predefined aims in reference to P-recovery from sewage sludge has led to a multitude of suggestions for suitable process parameters that must be addressed in future bench- and pilot-scale experimental runs.

Keywords: gasification, sewage sludge, agricultural residues, bed material, fluidized bed, feldspar, ash transformation, potassium, phosphorus, ICP-AES/MS, SEM, EDS, XRD, thermodynamic equilibrium modeling

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Appended Papers

Paper 1:

Layer Formation on Feldspar Bed Particles during Indirect Gasification of Wood. 1. K–Feldspar

Robin Faust, Thomas Karl Hannl, Teresa Berdugo Vilches, Matthias Kuba, Marcus Öhman, Martin Seemann, and Pavleta Knutsson

Author's Contribution: The author performed the thermodynamic equilibrium calculations, contributed in the selection of suitable analysis methods, and was part of the collaborative evaluation process.

Paper 2:

Layer Formation on Feldspar Bed Particles during Indirect Gasification of Wood. 2. Na–Feldspar

Thomas Karl Hannl, Robin Faust, Matthias Kuba, Pavleta Knutsson, Teresa Berdugo Vilches, Martin Seemann, and Marcus Öhman

Author's Contribution: The author performed the analysis, created the data sets, contributed in the selection of suitable analysis methods, and wrote the paper.

Paper 3:

Thermochemical equilibrium study of ash transformation during combustion and gasification of sewage sludge mixtures with agricultural residues with focus on the phosphorus speciation

Thomas Karl Hannl, Hamid Sefidari, Matthias Kuba, Nils Skoglund, and Marcus Öhman

Author's Contribution: The author performed the thermodynamic equilibrium calculations, selected the evaluation methodology, performed the result evaluation, and wrote the paper.

Paper 4:

Ash transformation during single pellet combustion using sewage sludge and mixtures with agricultural residues with a focus on phosphorus

Gustav Häggström, Thomas Karl Hannl, Ali Hedayati, Matthias Kuba, Nils Skoglund, and Marcus Öhman
Manuscript

Author's Contribution: The author contributed to the planning and execution of the experiments, performed the analysis in collaboration with the co-authors, and collaborated with the first author in the writing of the paper.

Paper 5:

Ash transformation during single pellet gasification of sewage sludge and mixtures with agricultural residues with a focus on phosphorus

Thomas Karl Hannl, Gustav Häggström, Ali Hedayati, Matthias Kuba, Nils Skoglund, and Marcus Öhman
Manuscript

Author's Contribution: The author contributed to the planning and execution of the experiments, performed the analysis in collaboration with the co-authors, performed the thermodynamic equilibrium calculations, and collaborated with the second author in the writing of the paper.

Abbreviations and Symbols

BFB	Bubbling Fluidized Bed
BSE	Backscattered Electron(s)
CFB	Circulating Fluidized Bed
d.a.f.	Dry Ash Fraction
d.f.	Dry Fuel
DFB	Dual Fluidized Bed
EDS	Energy Dispersive Spectroscopy
ICP–AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP–MS	Inductively Coupled Plasma Mass Spectroscopy
IMT	Initial Melting Temperature(s)
kt	Kilotons(s)
LM	Light Microscopy
mol.%	Molar Percentage
NLPM	Normal Liter(s) Per Minute
SEM	Scanning Electron Microscopy
SH	Sunflower Husks
SS	Sewage Sludge
SSH	Fuel Mixture of Sewage Sludge and Sunflower Husks
TEC	Thermodynamic Equilibrium Calculation(s)
TGA	Thermogravimetric Analysis
vol.%	Volume Percentage
WS	Wheat Straw
WSS	Fuel Mixture of Sewage Sludge and Wheat Straw
wt.%	Weight Percentage
WWTP	Wastewater Treatment Plant(s)
XRD	X–Ray Diffraction
XRF	X–Ray Fluorescence

Contents

Chapter 1

1   Introduction

Humanity's environmental impact and potential to alter the circumstances we live in have recently risen into the focus of research and legislation due to the public attention to this issue. Two of the most important issues are the elevated absorption of infrared radiation in the planet's atmosphere, mainly caused by elevated levels of the infrared-active gas CO_2, and the unsustainable consumption of resources with limited availabilities in the planet's crust. Ways of mitigating the greenhouse effect and making our resource consumption more sustainable are only effective if they include the majority of humankind. Therefore, supranational organizations and authorities have developed plans and directives to align our living standards with the planet's capacities.

Considering the global events that are likely caused or intensified by the ongoing climate change and our exploitation of the planet's resource boundaries, the current focus for this topic comes in late and needs to be intensified. This impression is strengthened since these issues have not been discovered recently but have merely been neglected for too long. The effect of CO_2 on the planet's atmosphere and our limitations in terms of certain resources were postulated decades ago [1–3]. The long-term negligence for this topic poses new problems for researchers since they need to improve the currently established systems rather than overthrow them and deploying completely new concepts.

One of these improvements was considering sewage sludge as a secondary resource instead of considering it as waste. This consideration has shed light on the potential of sewage sludge to function as an energy carrier for heat and electricity generation and as secondary raw material for the recovery of inorganic elements. While the recovery of energy and heat from sewage sludge has been enforced in many developed countries over the last years [4], a universal strategy for the recovery of inorganics from the created sewage sludge ash is not implemented yet. The element phosphorus (P) is especially abundant in sewage sludge ash and, therefore, the most prominent target element for potential recovery processes [5]. Recently, legislators noticed this recovery potential, which led to the development of directives and regulations stipulating phosphorus recovery from sewage sludge in the near future [6].

1.1   Phosphorus – a critical resource

Its crucial function causes the necessity to guarantee a continuous supply of P for living organisms as a DNA structure element, as a cellular energy transport agent, and as a hardener in vertebrates' bone tissue. The European Union classifies P together with phosphate rock as critical raw materials due to the dependence on imports of these resources and the necessity of P-based fertilizers to sustain the food production chain [7]. This evaluation conducted by the European Union also reveals that the contribution of material recycling to fulfill the supply demands is negligible for phosphate rock (17%) and inexistent for P (0%). Expanding the view

to a global scale, one may realize that the negligence of P-recycling processes implicates economic dependence on the primary reserves of phosphate rock, which are situated in the Western Sahara region (72%) and China (5%) [8].

Mined phosphate rock contains about 7-26 wt.% of P_2O_5, mostly in the orthophosphate form as apatite, but may also include significant amounts of hazardous impurities such as cadmium (Cd) and uranium (U) [9]. Since the P_2O_5-share in most mined phosphate ores does not suffice for the fertilizer industry, a sequence of pretreatment processes such as washing, screening, and various separation methods are applied to increase the P_2O_5-share to more than 28 wt.% [10]. Thereafter, P is extracted with acids from the rock, creating the precursor for basically every NPK-fertilizer product. These production stages are important to consider during the development of a P-recovery procedure since the quality of the recycled material defines its capacity to compete with the respective counterpart in the conventional production line. The aim of competitive P-recovery products should be the generation of a fertilizer or fertilizer precursor instead of creating a secondary resource with similar qualities to virgin phosphate rock.

A goal-oriented development of P-recovery streams primarily has to identify the main P-flows and P-rich waste streams. An evaluation of the pathway P follows from the phosphate ore to human consumption shows that humans consume only about 20% of the mined P due to significant side fluxes, e.g., erosion losses and disposal of P-rich wastes in the food production chain [11]. Optimizing these P-leaks would decrease the quantities of required P-resources more than any recovery process could do. Nevertheless, P-recovery should focus on the P consumed and subsequently excreted by humans as most countries collect and process this waste stream in wastewater treatment plants (WWTP). The existence of such centralized gathering compounds for wastewater facilitates the implementation of P-recovery processes. However, selecting a suitable P-recovery process is crucial and depends on the treatment that the wastewater undergoes.

1.2 **Current wastewater treatment processes**

The two most important output streams from conventional WWTP are freshwater, commonly seen as a valuable product, and sewage sludge, commonly seen as waste. Characteristically, the freshwater quality and purity are subject to a large amount of legislative regulation and, therefore, mostly equal when comparing different wastewater treatment plants [12]. The case is different for the sewage sludge constitution, which is defined by the input wastewater composition and the treatment agents used for the generation of the sewage sludge.

The impact of the incoming wastewater constitution on the development of P-recovery processes for the created sewage sludge is highly complex, but two main indicators may be identified. The first indicator is the total P-load in the wastewater. Since P is not added in the WWTP, the P-load is determined by the share of human extra and P-containing chemicals disposed into the sewage system [13]. The second indicator is the quantity of hazardous and toxic compounds in the wastewater. These compounds cover a wide range from harmful organic structures, e.g., hormones and pathogens, to toxic inorganic elements such as zinc, lead, and cadmium [14]. Considering both these aspects, efficient P-recovery processes should focus mainly on wastewater derived from domestic areas since the P-load correlates positively with the share of human excreta disposed into the wastewater system.

Domestic wastewater treatment is a complex process, including a series of mechanical, biological, and chemical separation methods [15]. To render the focus on the fate of P in this treatment process, only the possible pathways for P-removal from the water phase are elaborated here. The aim of the P-removal is the incorporation of P in the suspended solid phase and subsequent solids separation. This P-separation may be done by the chemical precipitation of the phosphates with coagulant agents. These agents are mostly salts, and their activity as precipitation agent is defined by the metal ion in the salt, functioning as a cationic chemical partner for the phosphates. Common metal ions functioning as precipitation agents are Ca, Fe, and Al. An alternative for the chemical precipitation is the biological P-removal, where P is incorporated in biomass structures by bacteria. The

important advantage of this alternative method is that the produced sewage sludge contains significantly fewer inorganics aside from P. Also, the sludge volume is decreased compared to the chemical precipitation method.[16]

Several different P-recovery processes may be applied at the WWTP after precipitating the P in the solid sewage sludge phase. These including adsorption, precipitation, and leaching processes to obtain (Al,Ca,Fe)-phosphates, calcium silicate hydrate (CSH), or magnesium ammonium phosphates (MAP) [17]. The main issue with these in-situ applications is comparably low P-recovery rates considering that >90% of the P from the input wastewater are available in the sewage sludge [18]. Furthermore, after P-removal, the remaining sewage sludge has still to be dealt with, since landfilling as a disposal option is prohibited or phasing out in most European countries [19]. Potentials to achieve higher P-recovery rates and deal with the sewage sludge volumes and its hazards have been found in the thermal conversion of sewage sludge combined with P-recovery from the thereby created sewage sludge ashes.

1.3   Thermal conversion of sewage sludge

The combustion and gasification of sewage sludge is a commonly employed technology in the European Union [20]. The benefits of thermal sewage sludge conversion include the recovery of energy or valuable organic compounds [21], the thermal decomposition of potentially harmful organic compounds such as pathogens and hormones [22], the selective separation of heavy metals as a function of the process parameters [23], and the decreased volume of a sanitized waste material that may be landfilled subsequently. Furthermore, conventional conversion processes of sewage sludge display retention of most of the inherent P in the coarse ash fraction [24]. However, thermal processing under reducing conditions at temperatures above 1500°C may transfer the majority of the P into the gas phase [25]. Within the possibilities for selecting a suitable conversion system, one of the most common technologies is the mono-conversion of sewage sludge in fluidized bed reactors due to the high fuel flexibility and the high conversion rate in these processes [26,27].

The thermal processing in fluidized bed systems comprises additional characteristics that need to be considered. The composition and constitution of the inorganics in fluidized bed systems play a major role since agglomeration processes may cause defluidization of the bed [28,29]. Additionally, the use of a bed material as heat carrier in fluidized bed systems makes the selection of a suitable bed material necessary. This selection has to factor in potential chemical interaction with the fuel, thermal and physical stability properties, and potential influences on the fuel conversion. Commonly used bed materials are quartz and olivine. Olivine is mainly used in fluidized bed gasification processes due to the beneficial catalytic effect for the syngas quality [30]. However, both these bed materials have properties with detrimental effects for the process. Quartz has shown problematic behavior leading to bed material fragmentation and bed agglomeration due to the reaction with ash–derived elements [31–33]. Olivine contains minor amounts of heavy metals such as Cr and Ni that can contaminate the ash fraction derived in the fluidized bed process, which has been observed previously [34].

P-recovery processes from sewage sludge ashes benefit from several aspects of the thermal conversion process. The retention of P in the ash fraction combined with the release of all or most of the organic structure means that the concentration of P in the ash is higher than in the sewage sludge. Furthermore, the separation of volatile heavy metals from the ash increases the quality of the ash for P-recovery, which is often expressed as a ratio of P and individual heavy metals, e.g., P/Cd [9]. However, the volatilization of heavy metals poses additional challenges for the flue gas or product gas treatment. More important aspects are the three T's temperature, turbulence/mixing, and time and the gas conditions in the thermal conversion process. Together with the presence of other ash–forming elements, these parameters determine the P-speciation, i.e., the cationic environment of P in the ash created by the thermal conversion process. Hence, the possibilities to alter the P-speciation in sewage sludge ash showed that the proper implementation of these parameters dictates the pathway of efficient P-recovery from sewage sludge ashes [21,35,36].

1.4 **Composition and behavior of sewage sludge ash**

Generally, the ash chemistry potential in thermal conversion processes depends heavily on the shares of the fuel's main ash–forming elements [37]. This perception is especially true and noteworthy for sewage sludge, which may be subject to significant fluctuation in its ash composition influenced by the spatial origin and production season. Possible influencing factors are the presence of industries or large non–domestic wastewater producers in the area and the seasonal fluctuations of the number of residents, e.g., in touristic regions [38,39].

Table 1 shows the mean and the range values for the composition of sewage sludge ashes from German sewage sludge treatment facilities. The displayed data set emphasizes that mean values taken for a bulk of different sewage sludge samples might be misleading when one tries to base its assumptions about the underlying ash chemistry on these values. The deviations in sewage sludge ash compositions are multivariate, but most of the extreme variations are by no means random. Exemplarily, the ashes with the lowest P–shares are derived from industrial sewage sludge ashes with little contribution by physiological P–sources. The highest Al–content is attributed to a specific facility that uses only Al–containing precipitation agents [38]. Therefore, it must be stated that any kind of P–recovery process has to be adaptive to or independent from the ash composition of the sewage sludge that shall function as a resource pool. Analysis of the fuel composition is of vital importance for this purpose.

With respect to the individual elements in sewage sludge ash, the origin and probability of occurrence in high quantities may be discussed. In general, sewage sludge ash is comparably alkali–lean (Na,K). It may contain a significant share of elements that are usually considered trace elements in biomass fuels, e.g., Ti, Mn, Zn, and Ba. The Mg–content is low within small ranges, mainly because neither the wastewater nor the treatment adds significant amounts of Mg. In contrast, the content of Al, Fe, and Ca is high and within large ranges caused by the use of different additives in the sewage sludge treatment process in a specific facility. The S–content in the sewage sludge depends on the presence of organically bound S and the use of sulfate precipitation agents. The presence of Si in sewage sludge

ash correlates mostly with the presence of sand and zeolite structures in the sewage sludge [27]. As mentioned, the P-content is driven by excreta and detergents in the wastewater, which is pointed up by the increased mean P-share of 9.0 wt.% if solely municipal WWTP's are considered.[38]

Table 1: Mass fractions and annual mass flows of the main elements in German sewage sludge ashes based on samples from 252 WWTP's. Table adapted from Krüger et al. [38].

Element	Min.	Max.	Mean	Annual mass flow
	wt.% d.a.f.			kt/year
Na	0.2	2.6	0.7	2.4
Mg	0.3	3.9	1.4	4.1
Al	0.7	20.2	5.2	15
Si	2.4	23.7	12.1	38.6
P	1.5	13.1	7.3	18.8
S	0.3	6.9	1.5	6
K	<0.1	1.7	0.9	2.2
Ca	6.1	37.8	13.8	42.7
Ti	0.1	1.5	0.4	1.3
Fe	1.8	20.3	9.9	29
Mn	<0.1	0.6	0.2	0.5
Zn	<0.1	0.5	0.3	0.8
Ba	<0.1	1.4	0.2	0.7

In addition to the total ash composition, the P-containing compounds present in the ash are crucial for P-recovery strategies. According to previous explanations, the P-compounds in the sewage sludge fuel depend on the used precipitation agent. Due to the dominance of chemical precipitation methods, most of the P in sewage sludge is present in the form of (Al, Ca, Fe)-phosphates [5,40]. Studies on these phosphates' plant availability postulate that they display a limited and slow uptake by plants [41]. It must be noted that this uptake is also affected by the plant type, soil acidity, and other factors. However, a preliminary conclusion derived by the P-speciation in sewage sludge is that an alteration of the P-species bound in (Al,Ca,Fe)-phosphates towards other phosphates is desired.

Studies focusing on the fate of P in thermal conversion processes of sewage sludge asserted that certain alteration processes occur due to the thermal treatment. The most pronounced mechanisms detected were the elimination of (Al,Fe)-phosphates during combustion and the formation of (Ca,Mg)-bearing orthophosphates correlating with Ca- and Mg-availability respectively [42–44]. The conclusion derived from most works focusing on sewage sludge ashes is that the substitution of the cations Al and Fe in the orthophosphate structures in sewage sludge is readily accomplished. However, the substituting element has to be present in the ash, its incorporation must be thermodynamically favored, and its state kinetically ready for reaction. Since most sewage sludge ashes offer mainly Ca as an alternative cation, Ca–phosphates with partial inclusion of other cation-forming elements are the favored compounds to be formed [24,38,45,46]. Regarding previous statements, the substitution of (Al,Fe)–phosphates with Ca-phosphates cannot be considered a significant upgrade since they display low plant-availability. Ashes dominated by Ca-phosphates as primary P-species can hardly be considered a fertilizer or fertilizer precursor, but merely a substitute for phosphate rock, which contains P in similar speciation [18].

1.5 **Alteration of phosphorus species in sewage sludge ash**

P-recovery from sewage sludge ashes often relies on considering the ash as secondary raw material with comparable P-content and P-speciation to phosphate rock. The question at hand is if there are possibilities to enhance the value of sewage sludge ashes by modification of the dominating phosphates of little plant availability. Research conducted on the plant availability of different phosphates stated that phosphates containing alkali elements such as Na or K have an improved capability to function as fertilizer [36,47,48].

Knowledge about this possibility to upgrade the P-recovery from sewage sludge led to the development of strategies and processes to achieve the incorporation of alkali elements in the phosphate structures derived from sewage sludge. Practical implementation of such processes dates back to the first half of the 20th century when apatite was thermally treated with

soda and quartz to obtain buchwaldite (CaNaPO$_4$) [49,50]. More modern practical implementations are the ASHDEC© P-recovery technology, where sewage sludge ash is processed with (K, Na)-salts to create Ca-(K,Na)-orthophosphates [48], and the MEPHREC© process, where sewage sludge is co-combusted with other P-rich wastes such as meat and bone meal [51]. Research focusing on the mechanisms responsible for this P-alteration has been conducted and gave insight into the driving factors for incorporating alkali elements into the phosphate structures [36,47]. Furthermore, the effect of the alkali amendments on plant–availability was studied in practice [52,53]. The studies could show that the reaction mechanisms of the sewage sludge ash and alkali additive are not limited to the phosphate compounds. Side reactions of the alkali element in the sewage sludge ash, mainly with Si compounds, imply that stoichiometric ratios between P and alkali element might not suffice the objective of (near) complete P-alteration [47].

Of the conclusions derived from the research conducted so far, one may conceive additional ways to recover valuable P-fertilizers and fertilizer precursors from sewage sludge ash. Based on the observation that alkali elements must be available at high process temperatures to alter the P-speciation, thermal co-conversion processes of sewage sludge with alkali-rich biomass fuels are possible ways rendering thermochemical post-treatment redundant. The possible types of alkali-rich biomass are numerous. However, biomass types with especially favorable characteristics are agricultural residues rich in K since they are annually generated and widely considered as waste stream [54]. Mixtures of sewage sludge and agricultural residues with the goal of P-alteration need to address the potential for side reactions of the K derived from the agricultural residue and the element quantities per mass of fuel. Considering the usual ash contents of the fuels and the combined elemental pool, agricultural residues presumably need to be the main fuel constituent in such mixtures.

The main aim when developing a co-conversion process of P-rich sewage sludge and K-rich agricultural residues is, beyond doubt, the alteration of the P-speciation directly during the thermal conversion process. How-

ever, the implementation of such processes could display additional desirable improvements to the process parameters. The co-conversion of ash-rich sewage sludge with agricultural residues could achieve higher power and heat output since agricultural residues have a higher average gross calorific value (GCV) than sewage sludge [55]. Furthermore, many ash-related issues with several agricultural residues such as ash melting and formation of corrosive volatiles may be inhibited [56,57]. However, the fundamental chemical aspects and mechanisms dominating the ash chemistry in these co-conversion processes are not fully understood today. Therefore, using fuel mixtures based on this concept must be preceded by a theoretical evaluation and lab-scale experiments to verify the analogies identified between the co-conversion of sewage sludge with agricultural residues and the commonly employed post-treatment processes for the generation of plant-available phosphates from sewage sludge ash.

1.6   **Objectives of this work**

The overall aim of the current work is to optimize fluidized bed gasification processes of sewage sludge and agricultural residues with the purpose of targeted formation and subsequent recovery of plant-available phosphates. Based on the current standard of knowledge and technologies, the generation of plant–available phosphates can potentially be achieved by the incorporation of K in the phosphate species. The cumulative work addresses both the influencing parameters of the ash composition and of the process conditions in fluidized bed gasification systems. A special interest of this study was to investigate parameters relevant to dual fluidized bed (DFB) gasification processes. More specifically, the objectives of this study were to determine:

- o   If feldspar is a viable bed material option in fluidized bed gasification systems to substitute commonly used bed materials with problematic properties in terms of heavy metal content (olivine) and process stability, e.g., bed agglomeration tendency and fragmentation (quartz)?   **Paper I & II**

- o   If mixtures of P-rich sewage sludge and K–rich agricultural residues have the potential to alter the P-speciation in the ash, and what role do the process parameters and the availability of other inorganic elements play?   **Paper III − V**

Chapter 2

2   Methodology

The results of this work are derived from various experimental and modeling approaches. The applied methods emphasize these differences in the reactor systems and fuels in large part. However, the objective of the used methodology was to set specific constants and variables between the different setups to enhance the comparability within the individual results. A detailed description of the employed methods can be found in the appended papers.

2.1   **Fuels**

The fuels used for this study include a variety of different biomass and waste resources.

The fuels used in Paper I & II were wood chips (WC) and wood pellets (WP). Both these fuels had a low ash content (0.4-0.5 wt.% d.f.). The ashes derived from wood chips and wood pellets mainly contained Ca, K, and Mg. The main difference between these two woody-type biomass fuels was the moisture content, about 8 wt.% for wood pellets and about 40 wt.% for wood chips.

Paper III implemented the composition of sewage sludge (SS1), wheat straw (WS), and sunflower husks (SH) in a thermodynamic equilibrium model. The SS1-fuel was derived from municipal wastewater treatment including precipitation and flocculation with Fe- and Al-agents. Therefore, its main ash-forming constituents were P, Fe, Si, Ca, and Al, which is a typical composition of municipal sewage sludge (see Table 1). WS was the representative fuel for a type of agricultural residues especially rich in Si and K. SH was representative for a different kind of agricultural residues as it was comparably Si-lean but rich in K, Ca, and Mg. In the model, the ash parameters were investigated as a function of the mixing ratio of these fuels.

Paper IV & V used the same type of fuels as Paper III but with slightly deviating compositions. The experimentally investigated fuels were pelletized pure sewage sludge (SS2), co-pelletized mixtures of sewage sludge with wheat straw (WSS10 & WSS30), and co-pelletized mixtures of sewage sludge with sunflower husks (SSH15 & SSH40). The appended number indicates the share of sewage sludge in the fuel mixture based on the dry fuels (d.f.). The specific mixing ratios were selected based on the ratio between the cation-forming elements Na, Mg, K, Ca and the anion-former P. The fuel mixtures WSS30 and SSH40 do not contain sufficient (K+Na) to substitute the (Al,Fe)-phosphate system completely. The fuel mixtures WSS10 an SSH15 contained a surplus of these cation-formers leading to the theoretical potential for a complete substitution of the (Al,Fe)-phosphate system.

The ash composition was obtained by different analysis methods, including ICP-AES and XRF, and the relevant main-ash forming elements are shown in Table 2. Additionally to these analyses, a SMT-protocol was

compiled for the SS2-fuel, determining the share of inorganically and organically bound P in the fuel to be 83% and 17%, respectively. The SMT-protocol also showed that 72% of the inorganically bound P was contained in non–apatite species.

Table 2: Main ash-forming elements and ash content of the fuels and fuel mixtures used in this research project. Values given in wt.% d.f. and mmol/kg d.f.

		Paper I & II		Paper III			Paper IV & V				
		WP	WC	SS1	WS	SH	SS2	WSS10	WSS30	SSH15	SSH40
Ash content [wt.% d.f.]		0.4	0.5	–	–	–	32.8	6.8	12.6	6.8	14.3
Na	mmol/kg d.f.	1	2	61	2	0	104	2	0	12	31
Mg		7	9	152	32	79	155	29	72	41	66
Al		1	1	482	5	1	561	6	1	58	169
Si		6	3	1068	337	17	1023	330	11	399	548
P		2	3	1291	21	24	934	19	23	107	297
S		6	3	380	22	46	378	20	39	53	126
Cl		3	3	28	59	11	27	57	10	54	47
K		10	21	66	216	191	100	210	190	196	181
Ca		25	32	873	71	95	678	69	89	127	257
Fe		1	0	1182	2	1	953	2	2	93	285
Ti		–	–	–	–	–	88	1	1	9	27
Mn		2	1	–	–	–	3	0	0	1	1
Other		–	–	–	–	–	18★	1★	1★	2★	6★

★ *indicates approximate complementary values; uncertainty due to lower detection limit*

2.2   Experimental Procedure

2.2.1   Pilot-scale indirect gasification experiments – Paper I, II

The reactor system used for the experiments in Paper I & II was the pilot-scale indirect gasifier situated at the Chalmers University of Technology in Gothenburg. The indirect gasification unit is depicted in Figure 1. The facility consists of a 12-MW circulating fluidized bed (CFB) boiler in connection with a 2-MW bubbling fluidized bed (BFB) gasifier. It can be run

as stand–alone CFB for heat generation or as coupled DFB reactor, in which the boiler provides heated bed material for the gasification process.

During the operation as DFB gasification unit, hot bed material from the CFB boiler (1) is precipitated in a cyclone (4) and subsequently collect in a particle distributor (9). From here, the bed material is forwarded into the gasifier (11), passing a loop seal (12) where sample may be extracted. Upon entering the gasifier, the separated particles function as bed material for the gasification process. Unconverted fuel and bed material exit the gasifier via loop seal 2 (13) and both are directed into the boiler, where unconverted fuel is burned and the bed material takes up heat again.

1. Furnace
2. Fuel Feeding (Furnace)
3. Wind Box
4. Cyclone
5. Convection Path
6. Secondary Cyclone
7. Textile Filter
8. Flue Gas Fan
9. Particle Distributor
10. Particle Cooler
11. Gasifier
12. Loop Seal 1
13. Loop Seal 2
14. Fuel Feeding (Gasifier)
15. Fuel Hopper (Gasifier)
16. Hopper
17. Fuel Hopper 1
18. Fuel Hopper 2
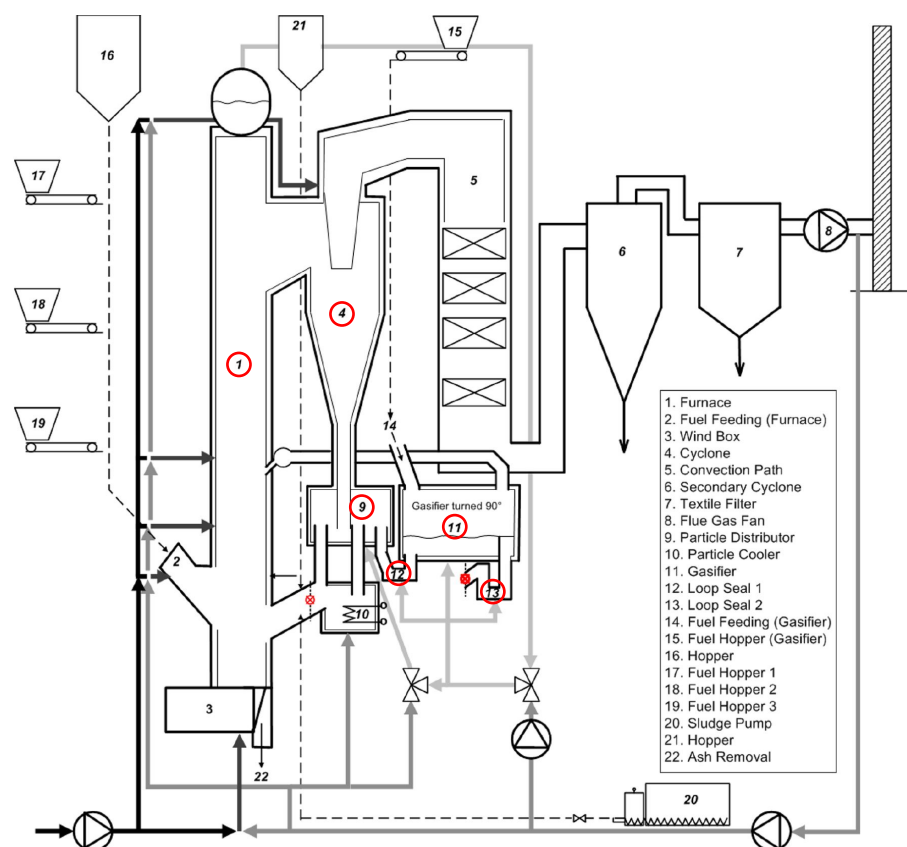19. Fuel Hopper 3
20. Sludge Pump
21. Hopper
22. Ash Removal

Figure 1: Schematic depiction of the Chalmers indirect gasifier used for the experiments in Paper I & II. Points of interest are marked in red. Adapted with permission from Larsson et al. [58]. Copyright 2013 American Chemical Society.

For this study, a mixture of K–feldspar and Na–feldspar was used as bed material. Impurities of Ca–feldspar and quartz in the bed material added up to about 12 wt.%. The chemical and mineralogical composition as given by the supplier is shown in Table 1.

Table 3: Elemental concentrations presented as oxides (left) and mineralogical composition (right) in/of the bed material used in the experiments of Paper I & II. [59]

Oxide	wt.%
SiO_2	67.0
Al_2O_3	18.7
K_2O	8.3
CaO	1.2
Na_2O	4.6
Other	0.2

Mineral	wt.%	Formula
K–Feldspar	48	$KAlSi_3O_8$
Na–Feldspar	40	$NaAlSi_3O_8$
Ca–Feldspar	6	$CaAl_2Si_2O_8$
Quartz	6	SiO_2

For the experiments, the CFB boiler was continuously run for 143 hours with a mixture of primarily wood chips and secondarily wood pellets at temperatures from 820-850°C. During daytime, the unit was run as DFB by operating the BFB gasifier with wood pellets and enabling bed material circulation between the reactors. Bed material samples were taken after 5, 23, 51, 76, and 143 hours at loop seal 1 and subsequently analyzed. The aim of this experimental setup was to determine the interaction of fuel ash and the feldspar bed material as a function of time.

2.2.2 Single pellet laboratory scale reactor experiments – Paper IV, V

Paper IV & V employed a single pellet lab–scale reactor that can be used for thermogravimetric analysis (TGA) situated at Luleå University of Technology for experiments converting sewage sludge (SS2) and mixtures of SS2 with the agricultural residues wheat straw (WS) and sunflower husks (SH). A schematic depiction of the TGA–reactor is shown in Figure 2.

The main components of the TGA–reactor consist of an externally heated cylindrical tube representing the conversion zone (height 450, diameter

100 mm), a gas inlet line where the gaseous compounds N_2, O_2, CO_2, and H_2O may be mixed and preheated, and a scale on top of the reactor which records the weight of the fuel sample attached via steel wire to the scale. The fuel sample in the experiments was a single pellet of the SS-fuel or the co-pelletized mixtures (WSS10, WSS30, SSH15, SSH40) at the time. The temperature in the conversion zone is monitored and manipulated based on the data recorded by a K-type thermocouple. Above the conversion zone there is a quenching zone where N_2 can be injected to avoid post-experimental reaction with atmospheric gases. In Paper IV, the conversion is operated under combustion conditions with a 7 NLPM gas mixture of 61 vol.% N_2, 4 vol.% O_2, 20 vol.% CO_2, and 15 vol.% H_2O at temperatures relevant for fluidized bed conversion, i.e. 800 or 950°C. In Paper V, the setup operated under gasification conditions with a 7 NLPM gas mixture of 65 vol.% N_2, 20 vol.% CO_2, and 15 vol.% H_2O at the same temperatures. After the conversion, the ashes were collected and analyzed.
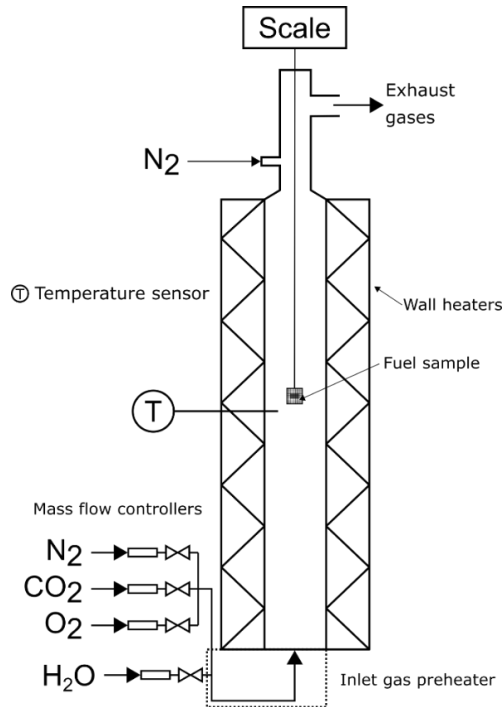

Figure 2: Schematic depiction of the Macro-TGA used in Paper IV & V.

2.3   Analysis Methods

2.3.1   Light microscopy – Paper IV

Optical characteristics of the ashes derived in Paper IV were determined by light microscopy (LM) with digital recording of images. The collected data gave insight into superficial aspects and the integrity of the ash matter. For the completed evaluation set of Paper V, a similar data set will be collected for comparative reasons.

2.3.2   SEM/EDS – Paper I, II, IV, V

All the experimentally produced ashes were analyzed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The facilities employed were a Phenom ProX SEM for top-view micrographs of bed material samples (Paper I), an FEI Quanta 200 FEG coupled with an EDS detector for cross-section analysis of bed material samples (Paper I), and a JEOL JSM-IT300 SEM equipped with an Oxford Instruments X-Max 80 EDS-detector for cross-section analysis and powder analysis (Paper II, IV, V). All the analysis facilities were used in backscatter-electron (BSE) detection mode, and the JEOL JSM-IT300 SEM operated at low-vacuum mode, i.e., 100 Pa.

The analysis procedure was focused on the representative collection of data regarding the morphology and elemental distribution across the ash samples and cross-sections, respectively. Therefore, the morphology was evaluated at certain magnification levels, and the data collection of the spatial distribution of elements included the same set of elements in all the analysis procedures (Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ti). The measurements were reprocessed to present the results on a C- and O-free basis. In Paper I and II, line scans were performed through the surface of the cross-sectioned bed materials to evaluate thickness and element distribution in the surface regions.

2.3.3   XRD – Paper I, II, IV, V

Two X-ray diffraction (XRD) facilities were used within this research work. For Paper I & II, the Siemens D5000 X-ray diffractometer using

Cu Kα radiation with a 2θ collection interval from 15° to 80° was utilized in combination with the ICDD PDF-4+ 2018 database for qualitative and semi-quantitative evaluation based on the reference intensity ratio (RIR). For Paper IV & V, a PANalytical Empyrean diffractometer using Cu Kα radiation and a Pixel3D array detector for the 2θ-range from 10 to 70° was employed with the specification of a 0.007° scanning step interval and dual–scan collection. The data in Paper IV & V was processed with the ICDD PDF-4 crystal database for qualitative compound characteriza-tion, and the Rietveld refinement analysis in conjunction with the K-factor method was used for compound quantification.

In Paper I & II, the XRD-results of bed material samples of different process ages were compared to determine the shift in crystalline phases from the starting point of the pure feldspar bed material. Paper IV & V analyzed the different ash fractions focusing on the alteration of phos-phates with the reference point of pure sewage sludge ash. Additionally, the Rietveld-analysis provided a quantification of the sum of amorphous phases in the ashes.

2.3.4 **ICP-AES/MS – Paper III, IV, V**

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and mass spectroscopy (ICP-MS) were used for the elemental characterization of the pure fuels in Paper III, IV, and V. The thereby collected data was the basis for the considerations related to suitable fuel mixtures and the thermodynamic equilibrium calculations.

Additionally, the ashes obtained in Paper IV & V were analyzed by ICP-AES/MS to evaluate the changes from the pure fuels to the generated ashes in terms of the inorganic elements. For this purpose, release rates of each inorganic element detected by the ICP-AES/MS were calculated according to Equation 1. The formula uses a set of values obtained during the experimental runs, including mass, water content, and concentration of the element i in the single pellet fed into the TGA (m_f, w_m^f, w_i^f) and the mass and concentration of the element i in the resulting ash (m_r, w_i^r).

Equation 1: Relative release rate R_i of the element i

$$R_i = 100 \times \left(1 - \frac{m_r}{m_f\left(1 - w_m^f\right)} \times \frac{w_i^r}{w_i^f} \right)$$

All the ICP-AES/MS analyses were performed by different external laboratories according to the quantification standards EN 15290 for the main ash-forming elements, EN 15297 for the minor ash-forming elements, and EN 15289 for Cl and S.

2.3.5 Thermodynamic equilibrium modeling – Paper I, II, III, IV, V

Thermodynamic equilibrium calculations (TEC) based on the concept of minimized Gibbs free energies were employed for the determination of the chemical speciation in thermodynamic equilibrium of the ashes (Paper I-V) and the bed materials (Paper I & II) analyzed in this research project. For this purpose, the software FactSage 7.2/7.3 was employed as interface for the integration of different databases. Paper I & II implemented the databases FToxid and FTsalt for the models of solid solution systems and FactPS for stoichiometric and gaseous compounds. Paper III, IV, and V implemented the database GTOX as primary database for solid solution models and SGPS as complementary model for stoichiometric condensed compounds and most of the gas compounds.

Paper I & II calculated the interaction potential of K-feldspar and Na-feldspar with the main ash-forming elements of the woody fuel, i.e. Ca and K. The calculations were carried out in combustion and gasification gas conditions in a temperature range from 600 to 1200°C. The extracted data from the calculations focused on the interaction of Ca and K with feldspar bed material, in reference to the interaction phenomena occurring in practice in surface near regions. Alterations of the feldspar minerals by reaction with ash elements and thereby changed melting behavior was determined quantitatively under the premises of thermodynamic equilibrium.

The aim of the thermodynamic modeling in Paper III was the determination of suitable mixtures of sewage sludge and agricultural residues with respect to the P-recovery potential. Therefore, the formation of melt, the P-speciation in the condensed phases and the precipitated melt, and the influence of the gas conditions with respect to the O_2 partial pressure were modeled as a function of temperature and the mixing ratio. Furthermore, the retention of the main ash-forming elements in the condensed ash phases was evaluated.

In Paper IV & V, TEC were employed for evaluating the thermodynamic state of the ashes generated in the experimental runs. The focus of the calculations was to determine the melting behavior and the P-alteration potential in the practically used mixtures and the influence of oxidizing and reducing gas conditions. The results derived by the model were compared with the experimental analysis results to identify the degree of equilibrium in the experiment and to obtain information about factors inhibiting equilibrium condition.

Chapter 3

3 Results and Discussion

Within this chapter, the main results and discussions stated in the appended papers are summarized, and the contribution of each individual paper to the general outcome and implications of this research project is addressed.

3.1 The applicability of feldspar bed materials

3.1.1 Layer formation on feldspar bed materials

Exposure of K–feldspar ($KAlSi_3O_8$) and Na–feldspar ($NaAlSi_3O_8$) bed material to woody biomass ashes dominated by Ca and K during indirect gasification resulted in distinctive interaction phenomena for K–feldspar and Na–feldspar, respectively. During the initial phase, the interaction of

the bed materials was mostly with ash–derived Ca. The initial layer formation on the bed material surface was driven by the reaction of Ca with Si in the feldspar structure, forming Ca-silicate ($CaSiO_3$) and Si–reduced feldspathoidal structures. This interaction was also suggested by the TEC models and supported by the XRD-analysis that detected an increasing share of $CaSiO_3$ throughout the experimental run. This Ca-rich layer grew in thickness and Ca-share over the exposure time. After 3 days, an additional layer on the outside of the Ca–reaction layer could be found, whose composition indicated that it mainly contained ash–derived elements with enrichment in those elements that do not react directly with the feldspar bed materials. The growth rate of these layers indicated that it was caused by deposition and diffusion in a solid–state diffusion model.

The main difference in the ash–bed material interaction between K–feldspar and the Na–feldspar was the formation of a K–enriched layer on Na–feldspars. This layer type was occasionally found in samples taken during the first days, but continuously in samples with higher exposure times than 3 days. These K–rich layers were only present on Na–feldspars, and they were situated between the Ca–reaction layer and the pure feldspar core. The K–share reached constant maximum levels of about 20 mol.% on a C– and O–free basis within these layers. Extended exposure time showed that these layers grew intensively in thickness over time without exceeding the aforementioned maximum K–shares. The levels of Al and Si in these layers indicate that K is replacing Na in the feldspar structure, whereby a feldspar or feldspathodial structure is maintained. This result was also obtained for the Na–feldspar in the TEC. The decreasing share of Na–feldspar in the XRD-results at higher exposure times supports this observation.

In addition to the layer formation phenomena, crack formation driven by the interaction of the feldspars with ash elements could be found. The cracks were seen in both feldspar types. Both the reaction with ash–derived Ca and K promoted the crack formation, which resulted in more extensive crack formation for Na–feldspar due to the reaction potential with K. The crack formation promoted the penetration depth of layer

structures on the feldspar bed materials. However, complete disintegration or particle fractionation did not occur quantitatively.

The results derived from Paper I & II gave insight into the stability and reactivity of feldspar bed materials during exposure to ashes dominated by the cation-formers Ca and K. The interaction with Ca and the deposition of ash matter on the outer surface was obtained for both Na–feldspar and K–feldspar, leading to crack formation and therefore decreasing the process stability. The reaction potential of Na–feldspar with fuel-K decreased its process stability even more due to chemical and physical bed material disintegration. This high chemical reactivity of Na–feldspar with K could be practically obtained in the SEM/EDS-analysis and the XRD-analysis, and it was thermodynamically supported by the TEC results. This work concluded that Na–feldspar is less stable than K–feldspar in conversion systems where K is available to react with the bed material. The main results concerning the time-dependent layer formation process on K–feldspar and Na–feldspar are schematically shown in Figure 3.
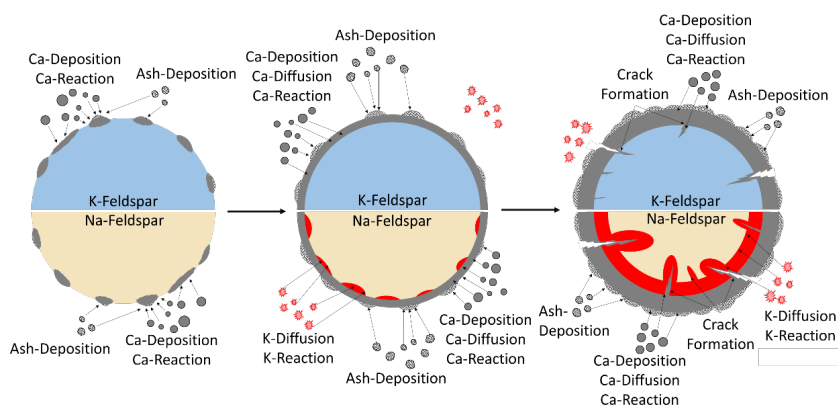

Figure 3: Schematic depiction of the time-dependent layer formation on (top) K-feldspar and (bottom) Na-feldspar due to exposure to wood ash in a dual fluidized bed system. Reprinted with permission from [60]. Copyright 2019 American Chemical Society.

Comparing the results obtained in Paper I & II with previously conducted research shows an agreement in large parts of the observations. The significance of Ca–diffusion and subsequent reaction with K–feldspar for the layer formation was obtained by He et al. during FB–combustion of woody biomass and by Wagner et al. during FB–combustion of bark and chicken manure [61,62]. The potential of the fuel ash to capture Ca that subsequently cannot react with the K–feldspar was mentioned was well. Furthermore, it should be stated that the formation of Ca–rich layers on bed material is partially desired as it may promote the syngas quality catalytically in gasification processes [63,64].

The formation of K–rich layers on Na–feldspars during thermal conversion processes has not been investigated in detail previously. However, research conducted on the thermochemically induced fractionation of Na–feldspar shows the possibility of K–reaction with Na–feldspar followed by crack formation and fractionation [65]. The interaction of Na–feldspar with K observed in this study can be especially problematic for biomass types that contain large amounts of K that is not captured by anion-formers in the ash.

3.1.2 Practical implications and comparison with commonly used bed materials

Several factors, like availability, chemical structure, durability, and heat conductivity, suggest that feldspars are technically and economically competitive with the used bed materials olivine and quartz. Furthermore, feldspars (but also quartz) are favored over olivine in conversion systems focusing on the recovery of ash resources since olivine contains environmentally harmful impurities such as Cr and Ni, which would be to the detriment of the recovered ash quality. Furthermore, an increased potential for tar reduction and water-gas shift was detected for fresh feldspar in comparison to fresh olivine in a previous work investigating the same process [66]. A comparison of feldspars and quartz needs to differentiate between K–feldspar and Na–feldspar and consider the specific conversion process. As both quartz and Na–feldspar experience significant reaction with K in thermal conversion processes, K–feldspar has the edge when K-

rich fuels are used. For pure sewage sludge conversion, this aspect might be unproblematic. However, in the suggested approach of P-rich sewage sludge co-conversion with K-rich agricultural residues, the interaction of K with the bed material instead of the interaction with sewage sludge phosphates would inhibit the desired effect of the fuel mixture. Therefore, K-feldspar appears to be a promising candidate for the application as bed material in sewage sludge co-conversion with agricultural residues.

The formation of Ca-rich layers could be verified for K-feldspar and Na-feldspar in analogy to olivine and quartz. Therefore, the use of feldspars as an alternative to quartz and olivine should maintain the gasification performance with respect to the catalytic effect of those layers that has been obtained previously [59,67]. Layer melting phenomena, possibly initiating bed agglomeration, were proposed by the TEC if the exclusion of K or Na from the feldspar structure may form layers where Na or K accumulate. These results indicate that the formation of alkali-silicate melts poses the biggest risk for bed agglomeration when using feldspar bed materials. Similar results have been obtained for quartz previously [31–33]. However, the experimental results showed that the required interaction with ash-derived K was only found for Na-feldspar. During the conversion with K-rich fuels it can be assumed that Na-feldspar is subject to a higher degree of layer melting and bed material fragmentation due to the reaction with K, comparable with quartz. The layer characteristics of K-feldspar resemble more the behavior of olivine, as the particle integrity is little affected by reaction with ash-derived K. Kuba et al. stated that the layers formed on K-feldspar are also less affected by layer fractionation than olivine layers [34]. No practical indication of agglomeration could be found in the corresponding experiments.

3.2 Phosphorus speciation during co-conversion of sewage sludge with agricultural residues

The potential for P-alteration during co-conversion of sewage sludge and agricultural residues was evaluated theoretically (Paper III) and practically (Paper IV & V).

3.2.1 **Behavior of phosphorus in thermochemical equilibrium**

The application of TEC represented the initial step to determine a setup viable for the formation and recovery of plant-available phosphates in co-conversion processes of sewage sludge and agricultural residues. By investigating the equilibrium ash constitution as a function of the fuel mixture, temperature, and the gas conditions during the conversion, the thermodynamic key parameters for melt formation, P-alteration, and compound precipitation could be determined. The used ash characteristics were typical for municipal sewage sludge (SS1), a K- and Si-rich agricultural residue (wheat straw, WS), and a K- and Ca-rich agricultural residue (sunflower husks, SH).

First, the ash composition in mixtures of sewage sludge with the agricultural residues was evaluated. The main observation of this evaluation was the dominance of sewage sludge ash elements in a wide range of fuel mixtures. This dominance was mainly caused by the comparably high ash content of sewage sludge. Considering the molar shares of main ash-forming elements, the ash content of sewage sludge was 7-12 times higher than the respective ash content of the agricultural residues. This implied that fuel mixtures with 50 wt.% or more sewage sludge in the mixture did not display a significant change in the ash composition. For the purpose of altering the chemical environment, agricultural residues had to be the main fuel compound. The difference between the agricultural residues in the fuel mixtures was mainly found to be the resulting balance of anion- and cation-formers, and therein especially the P/Si-ratio.

Subsequently, the melting behavior of the ash mixtures was analyzed by monitoring the initial melting temperature (IMT) and the share of ash elements incorporated in the melt as a function of temperature and fuel mixture under combustion and gasification conditions. The results showed that the influence of the gas conditions was mainly an increasing melting tendency of sewage sludge ashes under reducing conditions. This was mainly caused by the presence of Fe^{2+}-compounds in the condensed ash phase, which seemed to trigger the initial melt formation and subsequent incorporation of other ash elements at lower temperatures. The

addition of agricultural residues to the sewage sludge fuel shifted the melt-ing tendencies towards higher temperatures in mixtures containing up to 80 wt.% of agricultural residue in the fuel mixture. When higher amounts of agricultural residue were added, the trends for WS and SH diverged. While WS-ash showed high melting tendencies due to the formation of low-melting K-silicates, SH-ash showed little affinity towards melt for-mation due to the lack of anion-formers needed to establish an oxide melt. The presence and stability of carbonates in the SH-ash suggested that TEC not implementing a model for salt melts may underestimate the melting tendency of SH-ash.

The phosphorus speciation in the ashes of the fuel mixtures under com-bustion and gasification conditions was investigated at discrete tempera-tures relevant for thermal conversion processes. The P-speciation as a function of the ash-mixing ratio of the main ash-forming elements (α) is shown for different temperatures in Figure 4. The results indicated that both types of agricultural residues in the fuel mixture can create a chem-ical environment that favors the formation of K-bearing phosphates. The main difference between the agricultural residues was the enhanced in-corporation of P in the molten phase for mixtures of WS and SS compared to the mixtures of SH and SS. The effect of the gas conditions could also be observed in this analysis, as increased shares of P are present in molten structures under gasification conditions.

After generating data sets about the P-speciation at different process tem-peratures in the fuel mixtures of sewage sludge and agricultural residues, these data sets were used to predict the phases after cooling and precipi-tation of the ashes. The results showed that P contained in the molten phases predominantly precipitated in the form of K-bearing phosphates if the melt contained sufficient K to create those phosphates. This observa-tion was most obvious with the reference point of melt derived from SS-ash since this predicted melt contained only low amounts of K, and the mainly precipitated phosphates were (Ca,Mg)-phosphates and (Al,Fe)-phosphates. Most melts formed in the calculations were enriched in K in comparison to the bulk ash composition of the respective mixture. The

implication of this K-enrichment is that targeted melt formation may in-
crease the yield of K-bearing phosphates if the melt displays a beneficial
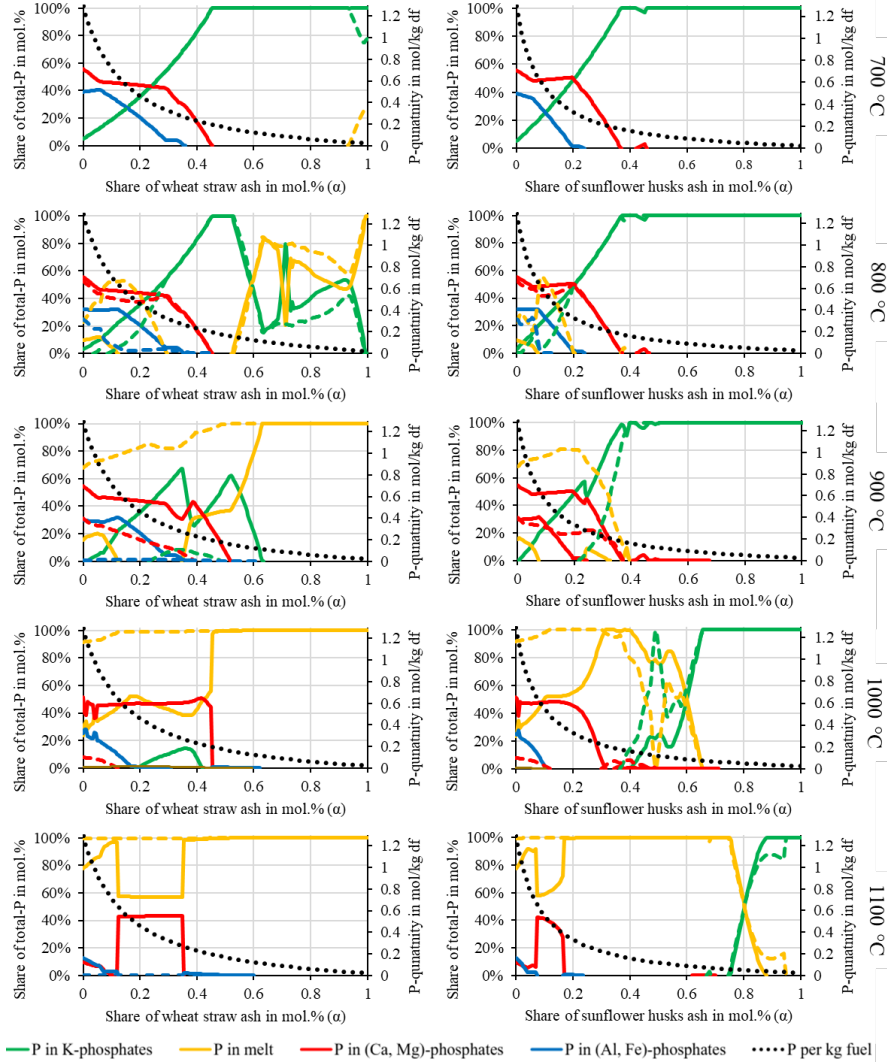composition for their formation during equilibrium precipitation.

*Figure 4: P-speciation for SS-mixtures with WS (left) and SH (right) at different tem-
peratures and under combustion conditions (continuous line) and under gasification condi-
tions (dashed line) in mol.% of total P. The total molar amount of P in the respective
fuel blend is indicated by the black dotted line in mol P/kg df.*

The TEC-approach to investigate the ash transformation chemistry during the co-conversion of sewage sludge and agricultural gave insight into mechanisms described previously in the literature and showed new aspects that need to be considered during experimental analysis. The role of alkali phosphates and Fe_2O_3-SiO_2-eutectics in the melt formation during sewage sludge combustion has been discussed previously [68]. Also, the melt formation due to low melting K-silicates in wheat straw ashes has been determined in many practical investigations [69,70]. While the melt formation due to K-silicates could be directly confirmed, the melt formation in sewage sludge ash in the TEC indicated that a surplus of P and the oxidization state of Fe played the major role in the initial melt formation. In terms of the P-alteration potential, the TEC supported the works mentioning that the formation of alkali-bearing phosphates is a favored mechanism when the chemical potential for this formation is provided in the ash [47,48]. However, in comparison to practical investigations, the TEC-results suggest that the formation of K-bearing phosphates is more dominant and almost unaffected by K-flux by volatilization or side reactions of K and P [24,47,71].

The most important differences to expect between this theoretical approach and experimental approaches are related to the assumption of equilibrium conditions. The experimental case must consider that a perfect fuel mixture as it is assumed in the calculations cannot be obtained, and the availability of the ash elements in reality is linked to their spatial distribution in the fuel mixtures, their state of matter in the respective chemical association and the reactivity of in its chemical environment. These factors affect the kinetics on the way towards thermodynamic significantly, with the implication that reaching thermodynamic equilibrium in the ash at the process conditions can hardly be considered a given fact. Subsequently, cooling and precipitation add the additional potential for non-equilibrium influences, such as the formation of amorphous structures. All of these differences need to be taken into account when deriving a conclusion from the TEC for the setup of experimental investigations.

3.2.2 Behavior of phosphorus in single-pellet experiments

After evaluating the theoretical potential for P-alteration during co-conversion of sewage sludge and agricultural residues in Paper III, experiments were conducted to determine the P-alteration potential in practice. The experimental approach used the same types of fuels as the theoretical approach in specific mixtures and investigated the influence of combustion and gasification conditions at temperatures relevant for fluidized bed conversion. The focus was on the practical potential to alter the P-speciation, the ash morphology, and the elemental distribution in the generated ashes.

The results of the elemental release analysis showed that both during combustion and gasification, no significant release rates for the main ash-forming elements Na, Mg, Al, Si, P, K, Ca, and Fe could be detected. In the contrary, S and Cl were almost completely removed from the condensed ash fraction formed in the single-pellet reactor. This observation agreed with the elemental release obtained in TEC for the used fuel mixtures. The result indicated that the formed ash had a composition that enabled the capture of potentially volatilized elements such as K, Na, or P. The release of S and Cl suggested that these elements may not form stable condensed compounds due to their comparably inferior thermodynamic stability. The elemental release analysis indicated that the interaction of elements derived from different individual fuels in the fuel mix was high.

Elemental distribution analysis across the bulk ashes showed that the assumption of homogenous ashes was misleading. Most ashes consisted of fractions that could be assigned to a specific original fuel due to their chemical composition. However, interaction phenomena could be detected in the morphological analysis and the elemental distribution. Interaction volumes between supposedly molten WS-ash and SS-ash could be found in the mixtures WSS10 and WSS30. A higher temperature and a higher share of WS in the fuel mixture increased the frequency of these interaction volumes. Regarding the elemental distribution, a very even distribution of K across the ashes could be found in comparison to the distribution of other main ash-forming elements. This regularity of the

K–distribution was the evenest in the SSH15–ashes, but it could be detected in all samples. Furthermore, Fe–exclusion phenomena could be found, most pronounced in the SS–ash. Higher temperatures and combustion conditions seemed to benefit this Fe–exclusion to the degree that combustion of SS at 950°C formed coating structures with more than 50 mol.% of Fe on a C– and O–free basis. Mineral structures could be found in the SEM–analysis of the ashes, and the presence of these minerals could be attributed to the SS–fuel. With respect to the fate of P, the SEM/EDS–analysis indicated that the association of P was still dominated by the interaction with elements derived from the SS–fuel. However, increased K–shares in the P–rich fractions and the formation of interaction volumes might benefit the aim of P–alteration.

The results of the XRD–evaluation supported several observations made in other analysis steps. Most importantly, the tendency of incorporating K into phosphate compounds either as substitution cation in whitlockites or by the formation of the $CaKPO_4$–orthophosphate could be obtained. These K–bearing phosphates were only found in the mixtures rich in agricultural residues, i.e., WSS10 and SSH15. Considering the elemental composition of these fuel mixtures, it seemed that a large surplus of K was needed for K to be in incorporated in phosphate structures. Apparently, the effect of side reactions and the stability of already formed whitlockites in the SS–ash was higher than the TEC suggested. The XRD–results suggested that a large fraction of K is contained in K–Al–silicates. Concerning other chemical aspects of the ashes, the exclusion phenomena of Fe could also be found in the XRD–analysis, where Fe–oxides were found in every ash sample. Additionally to hematite, maghemite could be identified in the ashes derived from gasification processes. The presence of periclase, calcite, and several types of sulfates in the SSH15–samples suggested that the formation of equilibrium conditions had not been reached in these samples since the thermochemical potential of the used ashes showed that these compounds display lower stability than the reaction products with P and Si.

Table 4: Crystalline phases and amorphous phase (in wt-%) as identified by XRD in the ash samples produced under combustion and gasification (in brackets) conditions.

	800°C					950°C				
Sample	SS	WSS10	WSS30	SSH15	SSH40	SS	WSS10	WSS30	SSH15	SSH40
Phosphates										
$Ca_5(PO_4)_3OH$ (hydroxylapatite)	– (-)	4 (-)	– (-)	11 (13)	– (-)	– (-)	– (-)	– (-)	14 (-)	– (-)
$Ca_5(PO_4)_{.6}(SiO_4)_{.4}(OH)_{.6}$ (Si-apatite)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (18)	– (-)
Whitlockite (Fe-substitute)	23 (18)	– (-)	27 (23)	– (-)	– (-)	– (7)	– (-)	– (-)	– (-)	– (-)
Whitlockite (K-Mg-substitute)	– (-)	7 (11)	– (-)	10 (19)	– (-)	– (-)	13 (17)	– (-)	19 (19)	– (-)
Whitlockite (Mg-substitute)	– (-)	– (-)	– (-)	– (-)	– (26)	26 (-)	– (-)	– (22)	– (-)	– (-)
Whitlockite (Fe-Mg-substitute)	– (-)	– (-)	– (-)	– (-)	27 (-)	– (-)	– (-)	21 (-)	– (-)	28 (24)
$Ca_4(Mg,Fe)_5(PO_4)_6$ (Stanfieldite)	– (21)	– (-)	– (-)	– (-)	– (-)	– (38)	– (-)	– (-)	– (-)	– (12)
$AlPO_4$	– (-)	7 (7)	– (-)	– (-)	– (-)	10 (-)	5 (-)	8 (13)	– (-)	– (-)
$CaKPO_4$	– (-)	4 (5)	– (-)	6 (9)	– (-)	– (-)	– (-)	– (-)	9 (-)	– (-)
Silicates and aluminosilicates										
SiO_2 (quartz)	2 (5)	– (3)	1 (7)	1 (1)	6 (2)	8 (6)	1 (5)	3 (4)	1 (-)	1 (4)
SiO_2 (cristobalite)	– (-)	2 (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)
SiO_2 (tridymite)	10 (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)
$K(Fe,Al)Si_3O_8$ (sanidine)	4 (-)	– (-)	14 (-)	– (-)	– (16)	11 (-)	– (-)	– (-)	– (-)	15 (-)
$KAlSi_2O_6$ (leucite)	– (-)	– (9)	– (-)	– (-)	– (-)	– (-)	14 (20)	16 (16)	– (13)	15 (17)
$KAlSi_3O_8$ (microcline)	13 (-)	9 (-)	9 (16)	– (-)	20 (16)	– (-)	6 (-)	– (-)	– (-)	– (10)
$K_2MgSi_3O_8$	– (-)	– (★)	– (-)	– (-)	– (-)	– (-)	– (★)	– (-)	– (-)	– (-)
Others										
α-Fe_2O_3 (hematite)	14 (5)	3 (2)	11 (6)	5 (8)	14 (12)	22 (-)	5 (-)	10 (4)	5 (5)	18 (6)
γ-Fe_2O_3 (maghemite)	– (-)	– (1)	– (5)	– (-)	– (2)	– (10)	– (5)	– (6)	– (10)	– (12)
$K_2Mg_2(SO_4)_3$ (langbeneite)	– (-)	– (-)	– (-)	3 (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)
K_2SO_4 (arcanite)	– (-)	– (-)	– (-)	5 (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)
$CaCO_3$ (calcite)	– (-)	– (13)	– (-)	3 (5)	– (1)	– (-)	– (-)	– (-)	– (-)	– (-)
MgO (periclase)	– (-)	– (-)	– (-)	4 (8)	– (-)	– (-)	– (-)	– (-)	7 (7)	– (-)
$MgFe_2O_4$	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	– (-)	8 (-)	– (-)
Amorphous and non-quantified crystalline compounds	34 (51)	64 (49)	38 (43)	52 (37)	33 (25)	23 (39)	56 (53)	42 (35)	37 (28)	23 (15)

★ indicates that the compound was identified qualitatively, but could not be quantified.

Based on the results of the analyses conducted in Paper IV & V, the fate of P during both the combustion and the gasification experiments could be estimated. Figure 5 displays the attribution of the P-content in the generated ashes to the compounds identified in the XRD-analysis and the TEC. The graphs indicate that WSS10 and SSH15 are the only fuel mixtures that formed ashes rich in K-bearing phosphates in the single-pellet experiments. Comparing the fate of P in the experiments and in the TEC, it can be observed that none of the experimentally generated ashes reaches or exceeds the level of P-alteration obtained in the TEC. In every ash sample, except SS-800 under combustion conditions, a majority of P was found in the crystalline phases. However, results close to 100% for P in crystalline phosphates suggest that the XRD result quantification is subject to pattern interferences.

The results of the experimental evaluation of the P-alteration in co-conversion processes of sewage sludge and agricultural residues could identify possibilities and downsides that agree well with previously conducted research. The necessity of using a surplus of alkali to alter the P-speciation by alkali-incorporation was mentioned previously and is a technological standard [47,48]. Increasing the selectivity of the K-reactions in the ash may be achieved by decreasing the share of Si and Al in the fuel prior to the thermal conversion process. However, the removal of Si from the fuel could hamper the formation of K-silicate melt, thereby possibly increasing the kinetic restrictions in the ash reactions necessary to reach a higher degree of P-alteration. Recent works suggest that processing at higher temperatures linked with enhanced melt formation could benefit the P-alteration [71].
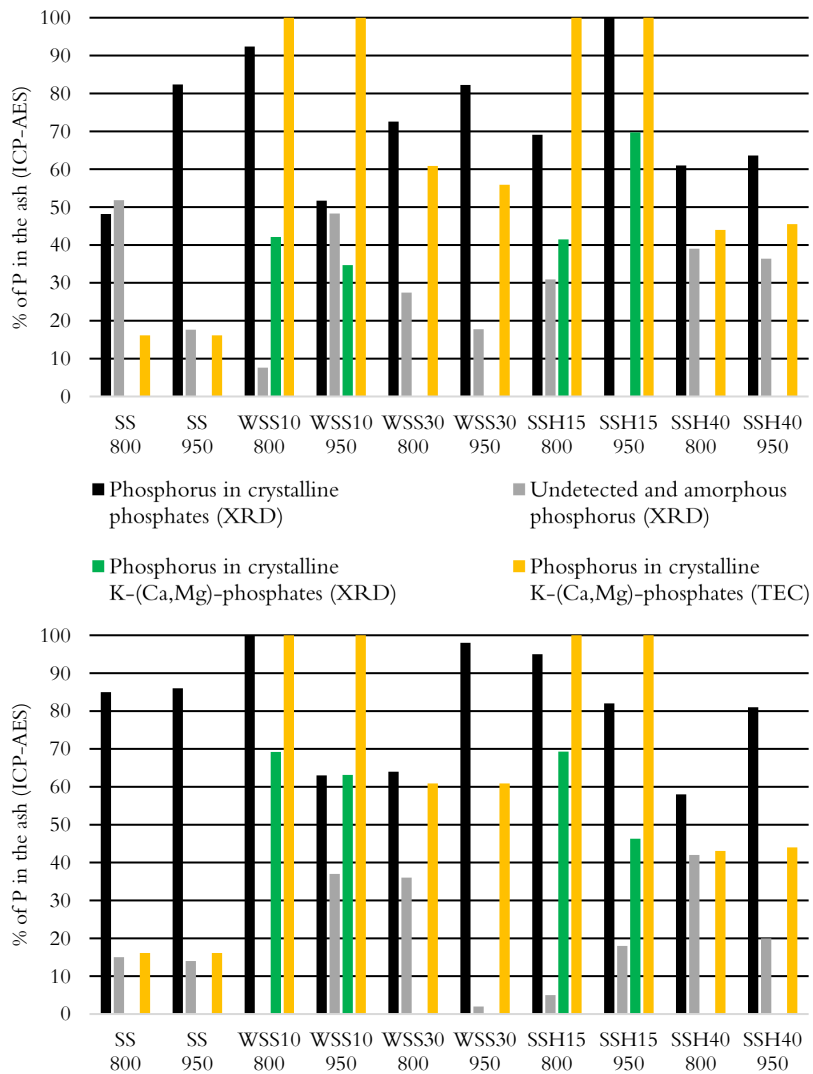
Figure 5: Estimated fate of P in the combustion experiments (above) and the gasification experiments (below). The estimation is based on the analytical data obtained by ICP-AES, XRD, and the TEC.

3.2.3 **Practical and future implications**

The results derived from this work revealed that the current standards for the ash analysis would benefit from additional methods and analysis refinement. Implementing closing conditions for the mass balance in the XRD-evaluation process could be helpful in case of peak interference to avoid misattribution. Furthermore, an analysis procedure for the currently uncharacterized amorphous fractions derived in the experimental research of the ash chemistry could improve the findings one could derive from such an experimental approach.

The results obtained in this research project conclude a set of aspects that needs to be considered in the practical design of fluidized bed sewage sludge conversion systems with agricultural residues with a focus on optimized P-recovery.

One of these aspects is the selection of an adequate bed material. An alternative for the most commonly used bed materials olivine and quartz is presented in this work and elaborated in detail in Paper I & II, i.e., K-feldspar and Na-feldspar.

Another aspect deals with the way of sewage sludge treatment prior to the thermal conversion. An important outcome of this research project was that the thermodynamic equilibrium conditions suggest a desirable crystalline ash speciation that was not obtained in the single-pellet experiments. This was mostly due to the formation of amorphous structures but is also affected by K being not selective towards the alteration of phosphates. A large fraction of K seems to be subject to side reactions, especially with Si and Al in the ash. A suggested way to improve the alteration of phosphates in co-conversion processes of sewage sludge and agricultural residues is to reduce the content of Si and Al in the sewage sludge. Since most of the K needed for the P-alteration is derived by the agricultural residue in the fuel mixture, this adaption could result in feasible fuel mixtures with a higher sewage sludge share.

With respect to the process performance of the used fuels, increased melting tendencies of the fuel mixtures, including sewage sludge and agricultural residues during gasification compared to combustion, were determined in the TEC. A corresponding result was unobtainable in the experiments, as the results lacked chemical information about the amorphous phase. The results indicate that exclusion phenomena, e.g., for Fe, occur to a lower degree in gasification processes, and the share of amorphous phases is increased. For a chemical evaluation, additional analysis methods to investigate the amorphous phases are needed and shall be implemented in future studies.

Furthermore, the large-scale implementation of the processes described in this work needs to be also evaluated with respect to legislative aspects. Agricultural residues dominated fuel mixtures suitable in the chosen P-recovery approach due to the high ash content of sewage sludge. It needs to be considered that the processes described in this work may not be fully covered by current legislation and directives regarding the proper treatment and disposal of sewage sludge. Compared to the currently most common technology for sewage sludge, i.e., mono-combustion, the co-conversion of sewage sludge and agricultural residues may require synergies in the legislation for different waste types.

The most important aspect with respect to the quality of the recovered ashes is the determination of the fertilizer applicability. Different standards have been developed to evaluate the plant availability of P, including standardized plant experiments and extraction methods. The focus should be on methods used to assess fertilizer products derived by post-processing of sewage sludge ashes, as these are the competitors for the ash generated in the co-conversion systems described in this work.

Chapter 4

4   Conclusions

Assigning the results obtained in this study to the outlined objectives and research questions derives the following main conclusions:

Objective 1: Is feldspar is a viable bed material option in fluidized bed gasification systems to substitute commonly used bed materials with problematic properties in terms of heavy metal content (olivine) and process stability, e.g., bed agglomeration tendency and fragmentation (quartz)?

- Layer formation on feldspar bed materials may create Ca-rich layers similar to quartz and olivine during indirect gasification with fuels that may provide Ca in their ash. The catalytic effects that are attributed to these layers can be expected.

- Na–feldspar displayed inferior process stability during the conversion due to enhanced interaction of the feldspar with K. This interaction did not occur with K-feldspars. This result implies that for the conversion of K-rich fuels, K-feldspar is preferable.

- In co-conversion processes of sewage sludge and agricultural residues, the desired outcome is the possibly selective reaction of K with phosphate compounds. Since Na–feldspar would probably decrease this selectivity and its process stability could be affected negatively, K-feldspar should be the preferred bed material.

- Compared to quartz, K-feldspar displays higher process stability and a lower bed agglomeration tendency when the fuel provides large amounts of reactive K in its ash.

- Compared to olivine, the layer formation and process stability are similar for K-feldspar, with the main benefit of K-feldspar not containing heavy metals such as Cr and Ni that are present in common olivine bed materials.

- The comparison of K-feldspar, Na–feldspar, quartz, and olivine based on this study and a literature review suggests K-feldspar as the most viable option in fluidized bed co-gasification processes of sewage sludge and agricultural residues.

Objective 2: Do mixtures of P-rich sewage sludge and K-rich agricultural residues have the potential to alter the P-speciation in the ash, and what role do the process parameters and the availability of other inorganic elements play?

- Both the TEC and the experiments showed that P and K are mostly (both ≥ 90%) contained in the condensed ash fraction during co-conversion of sewage sludge and agricultural residues at temperatures relevant for fluidized bed conversion.

- Thermodynamically, the formation of K-(Ca,Mg)–phosphates is the preferred option for the fate of P during co-conversion of sewage sludge and agricultural residues.

- The ashes of fuel mixtures of sewage sludge and agricultural residues formed at 800°C and 950°C displayed a heterogeneous nature with an inhomogeneous spatial distribution of the main ash-forming elements.

- K was the evenest distributed main ash-forming element across the ash sample with respect to the original distribution in the fuels.
- The high mobility of K across the bulk ashes in the experiments may facilitate the alteration of P derived from the sewage sludge.
- Experimentally generated ashes were dominated by whitlockite-type phosphates. These phosphates contained K as a substitute cation if sufficient agricultural residues were in the fuel mixture.
- P-alteration towards $CaKPO_4$, which was highly favored in the TEC, could be found in the ashes of the fuel mixtures containing the highest amounts of agricultural residues after combustion and gasification experiments.
- Higher process temperature favored the exclusion of Fe in the sewage sludge ash as Fe-oxide in the experiments. The TEC suggest that gasification conditions hinder this Fe-exclusion due to the inclusion of Fe in the formed melt.
- The formation of K-silicates and K–Al-silicates has been found in the experiments and the TEC. These compounds comprised the main fraction of K in the experiments, whereas in the TEC, they were thermodynamically subordinated to K-bearing phosphates.
- Effects detrimental to alteration of P in the ashes determined in this study include kinetic restrictions and the heterogeneous spatial distributions of the elements in the fuel mixture ashes.
- Side reactions of K and the stability of already formed phosphates in sewage sludge or sewage sludge ash played a major role in the experimental runs.
- The formation of K-bearing phosphates required a surplus of K to compensate for side reactions and non–equilibrium effects.
- A significant effect of the gasification conditions on the P-speciation and the available elements in the ash was not identified in the direct comparison of the experiments. The main influence of the atmosphere was on the fuel conversion time and the peak temperatures in the fuels in this study.

Chapter 5

5   References

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