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

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Abstract

The necessity of recycling anthropogenically used phosphorus due to depleting quantities of available phosphate ores encouraged recent research to identify potential alternative resource pools. One of these resource pools is the ash derived from the thermochemical conversion of sewage sludge. This ash is rich in phosphorus, although most of it is chemically associated in a way where it is not plant available. The purpose of this work was to identify the P-recovery potential of ashes from sewage sludge co-conversion processes with two types of agricultural residues, namely wheat straw (rich in K and Si) and sunflower husks (rich in K), employing thermodynamic equilibrium calculations. The results indicate that both the melting behavior and the formation of plant available phosphates can be enhanced by using these feedstock mixtures in comparison to pure sewage sludge feedstock. This enhanced bioavailability of phosphates was mostly due to the predicted formation of K-bearing phosphates in the mixtures instead of Ca/Fe/Al-phosphates in the pure sewage sludge ash. According to the calculations, gasification conditions could have a negative effect on the melting behavior of the mixtures dominated by the sewage sludge ash. Furthermore, the possibility of precipitating phosphates from ash melts could be shown. It is essential to emphasize that the results of this theoretical study ought to be used with caution since non-equilibrium influences were not investigated. Nevertheless, the applicability of thermodynamic calculations in the prediction of molten and solid phases may motivate experimental research in the future.

1. Introduction:

Depleting natural resources and the ongoing growth of population require major changeovers in the future concepts of resource consumption and recycling. Phosphorus (P) is one of the resources, for which it is crucial to find ways of recycling soon, due to the limited amount of extractable phosphate rock in the Earth's crust as well as the irreplaceability of phosphorus in a variety of organisms such as plants and creatures¹. A way of decreasing the dependence on mined P-minerals is

to recycle P and thereby decrease the P-losses in the phosphorus balance. These losses have been identified to be mainly associated with accumulation in soils, landfilling and transfer of P into the hydrosphere². Feasible options for minimizing the P-losses are, therefore, the reduction of fertilizer application, the recovery of P from P-rich wastes and the centralized gathering of P-rich streams in specific facilities. The focus of this work is the potential of P-recovery from sewage sludge wastes. Increasing the recycling rate of P for a sustainable use means returning the P

in sewage sludge back to the plants, where it originated.

Sewage sludge represents a suitable source for P-recovery because of its high P-content. However, the association of P in sewage sludge ash derived from mono-combustion plants³ and the high content of environmentally harmful elements and substances^{4,5} limit the application of sewage sludge as fertilizer on arable land. A way of separating beneficial from harmful fractions in sewage sludge is combustion and gasification, followed by the use of the sewage sludge ash as fertilizer or fertilizer precursor. Through the thermochemical conversion of sewage sludge, harmful fractions can be destroyed (e.g., hormones or pathogens) or separated (e.g., heavy metals) from the coarse ash fraction that contains the main P-fraction⁶⁻⁸.

Sewage sludge ashes contain P-amounts in a similar range as in mined phosphate rocks, i.e., up to 30 wt% P₂O₅^{9,10}. Nevertheless, the association of P in the sewage sludge ash tends to be little plant available and requires additional preparation before being used as fertilizer¹¹. Potential methods to create plant available P-compounds from sewage sludge ash are subsequent thermochemical treatment with alkali-salts¹² and acidic or basic extraction³. Through the addition of alkali-salts, the compounds whitlockite (Ca₃(PO₄)₂) and apatite (Ca₅(PO₄)₃OH) in sewage sludge ash from mono-combustion plants, which are poorly plant available, may be transferred into alkali-phosphates such as CaNaPO₄, which are more readily taken up by plants¹². The formation of K-bearing phosphates during combustion processes, where K and P are available, was shown previously^{13,14}, as was the effect of K on the solubility and plant availability of P in the ashes¹⁵.

A possibility of forming plant available P-species directly during the thermochemical conversion is the co-conversion of sewage sludge with alkali-rich feedstock, which may produce alkali-containing

phosphates. The incorporation of alkali elements in the phosphates could potentially render additional thermochemical treatment redundant and might have the potential to extract fertilizer material directly from the thermochemical conversion process, provided that the previously mentioned separation of heavy metals could be achieved. However, the composition of these feedstock mixtures in the co-combustion systems might worsen the operational performance due to enhanced ash melt formation. The use of such feedstock mixtures in industrial plants should be preceded by a theoretical and experimental analysis of the main benefits and drawbacks, to guarantee process stability and predict the chemical association of P in the ash fraction.

The objective of this work is to predict the ash transformation chemistry focusing on the P-speciation in combustion and gasification processes using sewage sludge mixtures with agricultural residues, namely, wheat straw (K- and Si-rich) and sunflower husks (K-rich) by thermodynamic equilibrium calculations. The applicability of employed thermodynamic calculation databases (GTOX, FactPS) to predict the melting behavior of the feedstock ash is presented. The potential of altering the speciation of P towards the formation of more plant available phosphates using feedstock mixtures in comparison to pure sewage sludge is studied. The predicted influence of the gas atmosphere and the process temperature on the type of phosphates and the melt formation in the coarse ash fraction is investigated.

2. Methodology

Feedstock:

The input data for the thermodynamic calculations represent the molar ash fraction of a typical sewage sludge sample (SS), wheat straw (WS), and sunflower husks (SH). The SS-feedstock was precipitated

with both iron sulfate (FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$) and poly aluminum chloride ($\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$). For the application in the thermodynamic calculations, the compositions are converted into mol of elements per kg of dry feedstock substance and standardized, since most mixing ratios based on dry feedstock would be dominated by the SS-ash, due to the high ash content of sewage sludge. The elemental ash compositions of the three feedstocks are given in Table 1.

	SS (mol /kg df)	WS (mol /kg df)	SH (mol /kg df)
Na	0.061	0.002	0.000
Mg	0.152	0.032	0.079
Al	0.482	0.005	0.001
Si	1.068	0.337	0.017
P	1.291	0.021	0.024
K	0.066	0.216	0.191
Ca	0.873	0.071	0.095
Fe	1.182	0.002	0.001
Σ	5.175	0.686	0.408

Table 1: Ash-forming elements in the feedstocks sewage sludge (SS), wheat straw (WS) and sunflower husks (SH) given in mol per kg of dry feedstock (df)

Thermodynamic Modelling:

The thermodynamic equilibrium calculations are performed with the software

FactSage 7.3. The principle of calculations in this software is based on the assumption of global equilibrium between all input elements with formation of compounds and solutions according to the minimization of Gibbs energy in the system. The databases GTOX (stoichiometric compounds, solutions, gas species) and FactPS (stoichiometric compounds, gas species) are used. The applicability of GTOX for the modeling of ash chemistry in P-rich systems has been shown previously^{16,17}. The FactPS database is implemented to allow the formation of H-bearing stoichiometric compounds and gases. In the case of compound duplicates, the priority is given to GTOX, and the FactPS compound is suppressed. The calculations are focused on the description of an oxide melt formation. Therefore, the presence of a salt melt is neglected, and the elements S and Cl are omitted.

The input data in the FactSage Equilib-tool represents the ash composition of sewage sludge, wheat straw, and sunflower husks and mixtures of sewage sludge with wheat straw and sunflower husks individually. The sensitivity of the calculations to the number of different elements in the input data is investigated by adding both alkali elements Na and K as K. This simplification was made due to the small amounts of

Elements	
H, C, N, O, Mg, Al, Si, P, K, Ca, Fe	
Database – GTOX (solution models)	
MeO: <i>CaO, MgO, K₂O, Al₂O₃, FeO</i> OLIV: <i>(Ca,Fe,Mg)(Ca,Fe,Mg)SiO₄</i> Garn: <i>(Al,Fe)₂Ca₃Si₃O₁₂</i> MULL: <i>Al₂(Al,Fe,Si)O₅</i> CAO: <i>Ca(Al,Fe)₂O₄</i> LEUC: <i>K(Al,Fe)Si₂O₆</i> FSPA: <i>K(Al,Fe)Si₃O₈</i> MELM: <i>Ca₂Si(Al,Mg)(Al,Si)O₇</i> NAFH: <i>K(Al,Fe)O₂</i> Stoichiometric solid compounds	LIOS – <i>oxide melt containing:</i> <i>Mg, Al, Si, P, K, Ca, Fe, O</i> C3PL: <i>(Ca, Mg)₃(PO₄)₂</i> CMP: <i>(Ca,Mg)CaP₂O₇</i> C2F: <i>Ca₂(Al,Fe)₂O₅</i> ALPM: <i>(Al,Si)(P,Si)O₄</i> SIOM: <i>(Al,Si)(P,Si)O₄</i> K3PM: <i>K₄(Ca,Mg)P₂O₈</i> CORU: <i>(Al, Fe)₂O₃</i> Gases: <i>CO₂, H₂O, O₂</i>
Database – FactPS (stoichiometric compounds)	
Gas compounds	Stoichiometric solid compounds

Table 2: Elements, compounds, and solution models used for the thermodynamic equilibrium calculations in FactSage. Database compounds are given in italics.

Na in the feedstock ashes and to focus on the speciation of the more dominant elements. Since Na is mainly found in SS-ash and the availability of alkali elements is rather low in these ashes, Na and K are summed to simulate a total availability of alkali elements instead of both K and Na individually. For the modeling of the combustion system, the gas atmosphere is set to guarantee fully oxidized conditions in the ash (20 vol% CO₂, 15 vol% H₂O, 4 vol% O₂, N₂). Due to the lack of information on the exact atmosphere in gasification systems, the gasification calculations are performed at O₂-partial pressures of 10-12 atm. This guarantees the presence of non-fully oxidized ash compounds, but it is just a benchmark for future analyses. The ratios of CO₂/CO and H₂O/H₂ are set by the equilibrium in the gasification calculations. The elements and databases used in conjunction with the considered solution models are given in Table 2.

3. Results

Melt Formation:

The formation of melt was calculated and evaluated for the pure feedstocks and the feedstock mixtures (SS+WS, SS+SH) in the temperature range from 700 to 1400 °C. Due to the methodology, the calculated and therefore evaluated melt refers solely to the oxide melt in equilibrium. This oxide melt varies in composition depending on the feedstock mixtures. Pure SS-ash and ashes dominated by SS form a melt dominated by Si, P, and Fe. Towards higher shares of WS in the mixture, the dominance of especially Fe and P in the melt decreases and the melt is dominated by K-silicates. Towards higher shares of SH in the mixture, the dominance of Fe and P decreases as well, although the levels are significantly higher than those calculated for the WS-mixtures. The melt of SH-mixtures is dominated by K, Mg, and P, whereas Si represents a minor fraction

of the melt composition. Both the mixtures with WS and SH individually show a trend towards higher levels of K. The only significant difference between combustion and gasification conditions was observed for the ashes dominated by SS-ash. Under gasification conditions, the shares of Fe and Al in the melt composition are expected to increase in comparison to the combustion conditions, whereas the shares of P and K are expected to decrease.

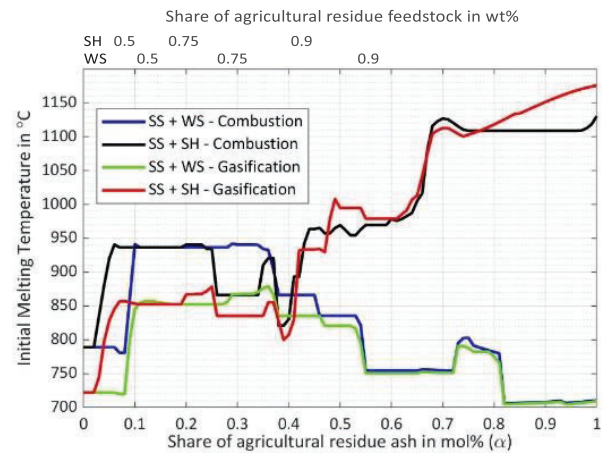


Figure 1: Initial Melting Temperature (IMT) of sewage sludge (SS) ash mixtures with wheat straw (WS) or sunflower husks (SH) under combustion and gasification conditions.

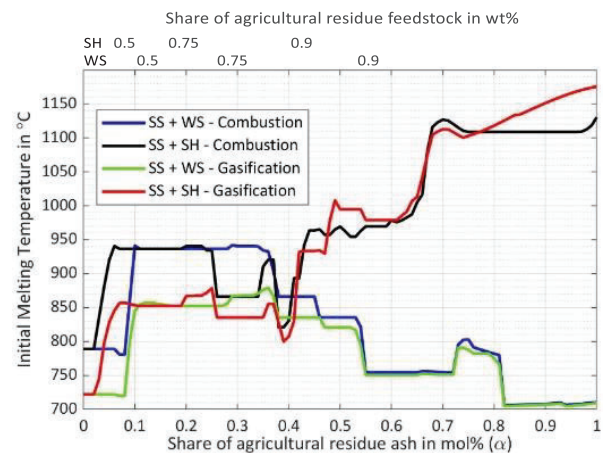


Figure 1 shows the calculated initial melt temperature (IMT) as a function of the feedstock ash mixture. The influence of the feedstock ash and the gas atmosphere can be seen. Starting from pure SS ($\alpha=0$), the IMT only depends on the gas atmosphere, with a significantly lower IMT under gasification conditions. The IMT increases for all mixtures and conditions when the share of SS-ash is decreased to

90 mol% (approx.. 50 wt.% SS in dry feedstock mixture). Towards higher shares of each agricultural residue respectively, the trends for combustion and gasification conditions converge for WS and SH respectively. Around 40 mol% of agricultural feedstock share (approx. 15 wt.% SS in dry feedstock mixture), the trends for SH and WS diverge, and the difference in atmospheric conditions becomes negligible. Towards the pure agricultural residues, the IMT mostly depends on the type of agricultural residue, whereas the gas atmosphere has an impact on the SH-mixture solely.

The melting behavior of specific feedstock mixtures is further analyzed to deepen the understanding of the melting behavior at higher temperatures. This analysis again showed a significant difference in both the feedstock mixtures and the influence of the gas atmosphere. The temperatures at which a certain fraction of the ash is present as a melt is shown in Table 3 for the pure feedstocks and specific mixtures under combustion conditions. The molar shares of the melt are given in terms of all condensed ash compounds excluding oxygen to set the focus on the chemical activity of the melt.

Feedstock	IMT (°C)	25 mol% Melt (°C)	50 mol% Melt (°C)	75 mol% Melt (°C)	100 mol% Melt (°C)
Pure SS	790 (725)	990 (860)	1100 (885)	1120 (900)	1355 (>1200)
Pure WS	715 (710)	715 (710)	725 (725)	740 (740)	900 (895)
Pure SH	1135 (1180)	1185 (>1200)	1400 (>1200)	1400 (>1200)	1400 (>1200)
80% SS 20% WS	940 (855)	940 (855)	990 (880)	1135 (905)	1305 (>1200)
60% SS 40% WS	870 (840)	870 (840)	870 (840)	1075 (905)	1255 (>1200)
40% SS 60% WS	755 (755)	755 (755)	820 (795)	980 (860)	1095 (980)
20% SS 80% WS	780 (765)	785 (780)	835 (825)	860 (845)	990 (945)
80% SS 20% SH	945 (870)	945 (870)	980 (880)	1075 (890)	1165 (980)
60% SS 40% SH	885 (815)	945 (935)	975 (945)	985 (995)	1020 (1080)

Table 3: Initial Melting Temperature (IMT) and the temperatures at which certain degrees of the condensed phases are present in the melt for the pure feedstocks and specific feedstock ash mixtures. The temperatures are given under combustion conditions and (in parenthesis) under gasification conditions. The analyzed T-increment was $\Delta T=5$ °C.

Comparing the pure feedstocks, WS had the lowest IMT, followed by SS and SH. An important characteristic of WS-ash was that a large fraction of the ash melted in a small temperature interval. In case of the SS-ash, the temperature gap until the majority of the ash melted was significantly larger. For the pure SH, the melt formation, including more than 50% of the

condensed phases was above the analyzed temperature interval (700-1400 °C). Notably, gasification conditions showed little effect on the melt formation in pure WS-ash, but at higher temperatures increasing negative effect on the melt formation in pure SS-ash. For the pure SH-ash, the effect of gasification conditions could not be

determined properly, because most melting processes occurred above the analyzed temperature interval. The negative impact of gasification conditions on feedstock ash mixtures dominated by SS-ash on one side and the negligible effect of gasification conditions on feedstock ash mixtures dominated by WS-ash are consistent with the findings for the pure feedstock ashes.

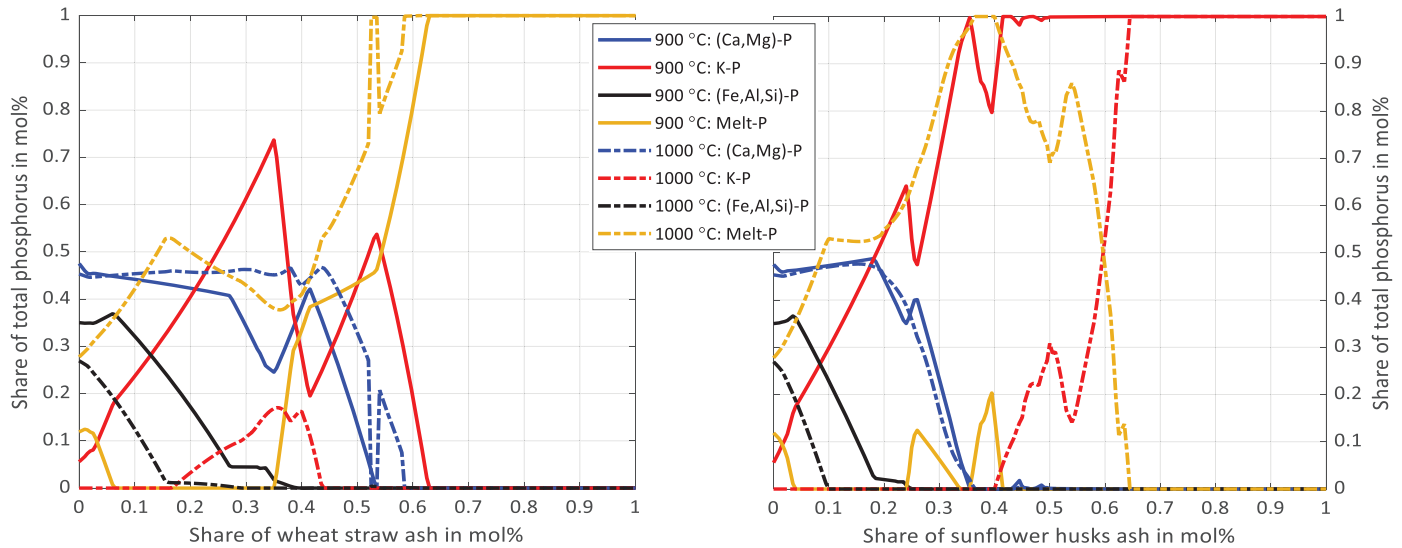


Figure 2: P-speciation for sewage sludge-mixtures with wheat straw (left) and sunflower husks (right) at 900 °C (continuous line) and at 1000 °C (dashed line) under combustion conditions.

Phosphorus Speciation:

The fate of P at specific process temperatures was analyzed in terms of the P-association with different groups of elements (Ca/Mg, K, Fe/Al/Si) and in the melt fraction. These groups may facilitate the determination of plant available P-fractions in future analyses. The grouping is focused on the accentuation of K-bearing phosphates, which means that the groups (Ca,Mg)-P and (Fe,Al)-P may incorporate additional elements such as Si but no K. All the K-bearing phosphates in the calculation, e.g., KMgPO_4 , $\text{CaK}_2\text{P}_2\text{O}_7$, CaKPO_4 , are subsumed under the term K-P. The P-speciation was analyzed for all feedstock ash mixing ratios in a temperature range of 700 to 1200 °C. A depiction of the P-association at 900 and 1000 °C for the mixtures with WS and SH respectively under combustion conditions is shown in

Figure 2. The figure and result presentation neglect all the compounds that do not contain P.

The results show that the P-speciation is strongly dependent on the temperature and the feedstock ash mixture. Pure SS-ash is dominated by phosphates incorporating Ca, Fe, and Al with minor amounts of P in the melt and K-rich phosphates. Along the WS-mixtures, the share of K-phosphates and molten P-compounds increases,

whereas feedstock ashes dominated by WS-ash contain just molten P-compounds. A similar trend can be seen for mixtures with SH-ash, although the ashes dominated by SH-ash do not contain molten P-compounds but only K-phosphates. The most significant difference in terms of the molten P-fraction is in mixtures with SH, where the share of melt-P is significantly higher at 1000 °C due to the formation of a K-, P-, and Si-rich melt. The influence of combustion and gasification conditions on the P-speciation was insignificant in the calculations.

Melt Precipitation:

As shown previously, a significant amount of P can be contained in the molten ash fraction depending on the conditions and the feedstock mixtures. Since these ashes will undergo a cooling process before any

further processing may be performed, it is of interest, which compounds precipitate from the melt under equilibrium cooling. Representatively for this analysis, the molten fractions of SS-mixtures with 50 mol% SH ash and 50 mol% WS ash, respectively at 1000 °C under combustion conditions are shown in Figure 3.

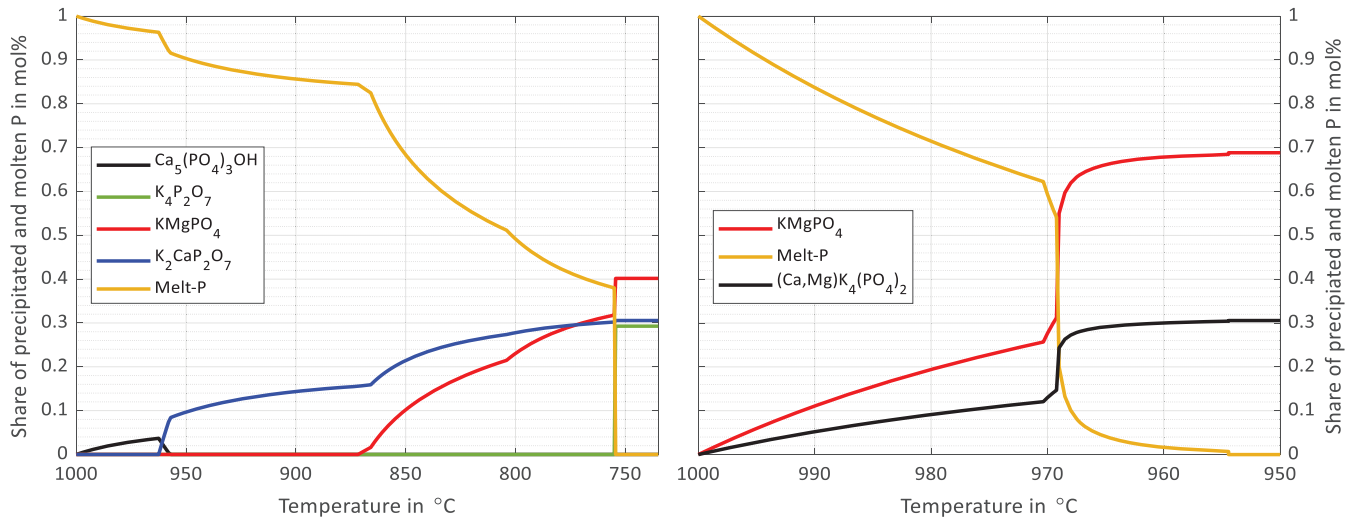


Figure 3: Precipitation of the melt fraction formed at 1000 °C under combustion conditions for mixtures of sewage sludge with wheat straw (left) and sunflower husks (right).

The outcome of the equilibrium precipitation analysis suggests that P in the melt precipitates almost solely as K-containing phosphate if sufficient K is available in the melt. For both of the presented feedstock mixtures, the melt is K-rich and phosphates are precipitated as K-bearing phosphates. Calculations of ashes dominated by SS-ash show that Ca-phosphates are expected to form if insufficient K is available. The data also shows that K-phosphates are preferred over K-silicates when K is the limiting factor in the melt composition. Precipitation under gasification conditions showed little impact on the P-speciation in the precipitated compounds.

4. Discussion

Melt Formation:

Interpretation of the results for the initial melting temperature (IMT) shown in Figure 1 is focused on the influence of the gas

atmosphere and the different feedstock compositions. The decreased IMT for all ash mixtures dominated by SS is correlated to the state of Fe-phosphates in the ash. The abrupt rise in IMT when approximately 10 mol% agricultural residue ash is present may be attributed to the formation of more stable phosphates and Fe-

oxides, which inhibits the incorporation of Fe and P into the melt. The decrease of Fe accompanied by the increase of K as the share of SS-ash decreases seems to favor the formation of more stable K-phosphates (e.g., KMgPO_4). Based on the different compound formation between combustion and gasification conditions, the oxidation state of the Fe-oxides (Fe^{2+} , Fe^{3+}) and formation of vivianite ($\text{Fe}_3(\text{PO}_4)_2$) may be the dominating factor for the decreased IMT under gasification conditions. This case is important to consider since a large fraction of P in precipitated SS can be bound to Fe^{2+} as vivianite¹⁸, an important resource for P-recovery¹⁹. The difference in IMT towards the pure SH and WS may be explained by the formation of low-melting K-silicates in the WS-ash, which has been documented in previous studies^{14,20}. In the equilibrium calculations, the Si-lean SH-ash tends to form ash enriched in CaO and MgO, which are highly stable up to higher

temperatures. Notably, the gasification atmosphere increased the IMT for high SH-shares in comparison to the combustion atmosphere because K was bound as carbonate, and higher amounts of K were volatilized as KOH. The presence of carbonates indicates that the calculations solely based on the formation of an oxide melt are insufficient at high shares SH-ash, and the formation of a salt melt should be considered. Previous research stated higher stability of K_2CO_3 in a Si-lean and CO_2 -rich environment ²¹. Detailed studies for the gaseous release of K would need to include Cl in the calculations ^{22,23}.

The analysis of the melting behavior provided in Table 3 indicates several effects of the feedstock mixing and the gas atmosphere, which may influence the thermochemical conversion process. The mixtures with sunflower husks and wheat straw melt up to 50 mol% in a small temperature interval. The composition data suggests that this result is caused by excessive inclusion of K and P in the melt, which is enhanced by further addition of K-rich agricultural feedstock. Previous research found that excess of P and K promoted the formation of low-melting phosphates ¹⁴. Although the initial melt formation was shifted towards higher temperatures, the melt starts to dissolve and incorporate a large fraction of silicates and phosphates soon thereafter. Total melting of SH-rich mixtures was inhibited by the formation of stable alkaline oxides (CaO, MgO).

In reality, the melting behavior of these feedstock mixtures might be significantly different from these theoretical equilibrium calculations due to various reasons. The assumption that in a feedstock mixture, every individual ash element is readily available to react or be associated in the melt is not reflecting the real capability of mixing technology. Even under perfect mixing parameters, the original feedstock will maintain its structure partially within

the mixture particles, which means that elements present in different pure feedstocks might not interact as freely as the calculations suggest. This interaction barrier should also be considered when highly stable solid compounds are incorporated in the melt in theory. Another aspect is that the interaction between solid compounds is considered to have no kinetic limitations in equilibrium calculations. The reactivity of the ash elements, in reality, will be defined by their state of matter. It needs to be considered that an individual pure feedstock fraction in the ash could melt or volatilize to enhance the interaction with the other feedstocks ash.

Phosphorus Speciation and Precipitation:

The results of the thermodynamic calculations at specific temperatures over the entire range of mixture ratios show the potential of using SS-mixtures with agricultural residues for the creation of K-bearing phosphates. The desired shift from Ca/Mg-phosphates and Fe/Al/Si-phosphates towards K-phosphates when using feedstock mixtures was identified. It could be shown that K-bearing phosphates are thermodynamically favored in a P-limited ash environment. Therefore, the calculations indicate that the entire P was present in K-bearing phosphates (or as molten P-compounds) when the agricultural residue ash was the dominating ash fraction. The results obtained for the P-association in this work are in accordance with previous findings of the possibility to change the P-speciation in sewage sludge ashes by adding alkali-rich additives ¹². Modeling a function of the P-species in dependence of a feedstock mixture, process temperature and gas atmosphere has shown its applicability in this theoretic approach. In conjunction with experiments, it would be possible to verify the results and obtain an approximation of how far experimental data deviate from equilibrium data.

Knowledge about the deviating factors between theory and experiment could establish a baseline to repeat such a methodology for other feedstock mixtures to investigate their potential of P-recovery.

The thermodynamic modeling of the P-speciation has to be evaluated critically too. First, the groups in terms of the P-associates (Ca/Mg, K, Fe/Al/Si) were selected subjectively to show the transition of the elements associated with P in the ash depending on the feedstock ash mixture and depending on the temperature. Furthermore, it was assumed that an individual group of phosphates shows similar behavior when applied as fertilizer. This approach neglects the role of the plant, the soil, and also the varying plant availability within one group²⁴. Additionally, the assumption of equilibrium in the calculations gives a simplified picture of the potential P-associations in the feedstock mixtures. The shift from Ca, Fe, and Al-phosphates towards K-phosphates is assumed to occur without kinetic limitations as a solid-solid reaction. In reality, the formation of K-phosphates will probably be enhanced by volatilized or K and P in the melt, whereas solid-solid reaction might be inhibited significantly. Furthermore, the calculations suggest that K-phosphates such as KMgPO_4 are the most stable phosphate form in this system. Therefore, the only phosphates occurring in P-lean feedstock mixtures are K-phosphates or, at higher temperatures, molten phosphates. This equilibrium assumption proposes that several other stable phosphates, which may have formed previously, e.g., $\text{Ca}_3(\text{PO}_4)_2$ would disintegrate to make P available for the reaction with excess-K. Considering the occurrence and stability of Ca-phosphates, this is probably not always the case in practice.

The potential of P-compounds precipitated from the molten ash fraction was identified in the equilibrium precipitation. Although the calculations indicate that molten ashes

of feedstock mixtures may precipitate mainly as K-phosphates, real precipitation cases might differ significantly. A major aspect that is lost in equilibrium cooling is the formation of amorphous material due to non-equilibrium phase transitions. Previous studies showed that amorphous material might represent a large fraction of condensed ash phases and the presence of other stable phosphates such as whitlockite ($\text{Ca}_3(\text{PO}_4)_2$), hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) or tridymite polymorphs of aluminum phosphate (AlPO_4) has been shown previously and needs to be considered^{11,25}.

5. Conclusion

Thermodynamic equilibrium calculations were performed to predict the ash transformation chemistry of sewage sludge mixtures with both sunflower husks or wheat straw under combustion and gasification conditions. Focusing on the melting behavior of the ashes and the speciation of P in the ash, the following conclusion may be drawn:

- The low initial melting temperature of sewage sludge ash, dominated by P, Fe, Si, Ca, and Al, increased significantly when the share of agricultural feedstock was above 50 wt% (approx. 10 mol% ash).
- Wheat straw (K- and Si-rich) and sunflower husks (K-rich) showed significantly different melting behavior when mixed with sewage sludge for thermochemical conversion. This difference is mainly attributed to the high shares of Si in wheat straw, forming a low melting K-silicate melt.
- Gasification conditions had the most detrimental effect on ashes dominated by sewage sludge ash. The melting tendencies during gasification were shifted towards lower temperatures for all feedstock mixtures where sewage sludge ash was dominant. The appearance of melt at lower temperatures was found to correlate with the

presence of Fe²⁺-compounds, especially vivianite.

- P in sewage sludge ashes in the calculations was mostly associated with Ca, Fe, and Al. When mixed with wheat straw or sunflower husks, the thermodynamic equilibrium shifted towards K-bearing and molten phosphates
- The precipitation of molten ashes showed high stability of K-bearing phosphates formed through equilibrium cooling.
- Alteration of the P-speciation in by co-conversion of sewage sludge with agricultural residues towards plant available phosphates was thermodynamically favored due to the high stability of K-bearing phosphates.

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The occurrence of such an alteration of the P-speciation might be highly limited by kinetic aspects, especially when the transition is suggested to be solely between solid compounds. Furthermore, the occurrence of amorphous ash material has to be considered under real (non-equilibrium) conditions. Therefore, this theoretical approach must be validated by an experimental setup to find the kinetic limitations and the non-equilibrium factors that are of relevance for the P-speciation in the ash.

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