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Fate of Phosphorus in Fluidized Bed Cocombustion of Chicken Litter with Wheat Straw and Bark Residues

Gustav Häggström,† Katharina Fürsatz, Matthias Kuba, Nils Skoglund, and Marcus Öhman

ABSTRACT: This study aimed to determine the fate of P during fluidized bed co-combustion of chicken litter (CL) with K-rich fuels [e.g., wheat straw (WS)] and Ca-rich fuels (bark). The effect of fuel blending on phosphate speciation in ash was investigated. This was performed by chemical characterization of ash fractions to determine which phosphate compounds had formed and identify plausible ash transformation reactions for P. The ash fractions were produced in combustion experiments using CL and fuel blends with 30% CL and WS or bark (B) at 790–810 °C in a 5 kW laboratory-scale bubbling fluidized bed. Potassium feldspar was used as the bed material. Bed ash particles, cyclone ash, and particulate matter (PM) were collected and subjected to chemical analysis with scanning electron microscopy–energy-dispersive X-ray spectrometry (SEM–EDS) and X-ray diffraction. P was detected in coarse ash fractions only, that is, bed ash, cyclone ash, and coarse PM fraction (>1 μm); no P could be detected in the fine PM fraction (<1 μm). SEM–EDS analysis showed that P was mainly present in K–Ca–P-rich areas for pure CL as well as in the ashes from the fuel blends of CL with WS or B. In the WS blend, P was found together with Si in these areas. The crystalline compound containing P was hydroxyapatite in all cases as well as whitlockite in the cases of pure CL and WS blend, of which the latter compound has been previously identified as a promising plant nutrient. The ash fractions from CL and bark blend only contained P in hydroxyapatite. Co-combustion of CL together with WS appears to be promising for P recovery, and ashes with this composition could be further studied in plant growth experiments.

1. INTRODUCTION

Phosphorus (P) is one of the main nutrients important for crop production and, therefore, also food production.1 Currently, the main source for P is produced from the ore mineral apatite that is extracted through mining and further processed into fertilizers.1 As with many other finite resources, there are concerns for the longevity of this mineral, and thus P has been identified as a critical raw material by the EU.2 P is identified as one of the planetary boundaries for a sustainable society, and leaching of P from arable lands increases the risk for eutrophication of nearby bodies of water.3

Manures are an example of P-rich residual stream4,5 which could be utilized more efficiently in P recycling. Today, manures are used as N, P, and K sources, but it might also facilitate organic pollutant transfer from animal farming to agriculture. Manures may also become a waste problem in regions with limited or no local agriculture close to animal farming.6,7 The excess manure in such regions may be considered as fuels in bioenergy systems as they have a significant organic content.8 Utilizing such excess manure, with no immediate recipient in agriculture, in a combustion process produces ash fractions that could be suitable for P recovery. The ash product, and inherent material reduction, facilitates transportation to other regions for further recovery processing or direct use as a fertilizer if the quality fulfills legislated demands. Combustion also addresses storage issues associated with excess manure, such as nitrogen leaching into groundwater and greenhouse gas emissions from bacterial activity during prolonged storage.9

Agricultural residues such as straws or husks are other examples of residual biomasses suitable as feedstocks in bioenergy conversion. A major challenge with the introduction of agricultural residues in combustion processes is their composition of inorganic constituents, mainly Si and K,4 which may form low-temperature melting compounds during combustion.8,9 This is especially crucial for the operation of fluidized bed boilers because of agglomeration, fouling, and deposit formation.10,11 Previous studies have shown the possibility to alleviate these problems using P additives and P-rich fuels.12,13 Residual streams of woody biomass are commonly used as a fuel for heat and power production in Europe, and the sources are typically wood unsuitable for construction, or pulp and paper, or industrial by-products such as saw dust or bark.14 Ashes from these wood-type fuels are generally rich in Ca, especially in biomass such as bark.4 As woody biomass is commonly used for bioenergy, today it can be used to compensate for the availability of various other biomass residues, and it is likely that woody biomass will be co-combusted with other feedstocks.

When co-combusting K- and Ca-rich fuels with P-containing fuels or materials, the speciation of P has been shown to vary.12,13 A large surplus of Ca in comparison to P will favor the
reactions toward the thermodynamically favored apatite, a compound which is largely unavailable to plants in the short time span relevant for annual crops.15 K-containing phosphates form when the K and P content is relatively high compared to the Ca content. However, the solubility of pure K phosphates mean that they are more prone to contribute to eutrophication in adjacent bodies of water than, for example, apatite.16 Previous research on phosphates in ash fractions indicate that whitlockites incorporating K in the crystalline structure have leaching properties that make these phosphates suitable for plant uptake.17

Understanding the phosphates that could form in combustion processes is facilitated by the so-called ash transformation reactions.18 Ash reaction pathways can be described using primary, secondary, and tertiary reactions if the elements in the fuel are assumed to exist as nonmineralized materials.19 If the elements are already associated in the biomass, the reaction pathway is dictated by the strength of those bonds.18 In the oxidizing P case and for fuels where P is organically associated with the fuel, this would suggest that any P that is initially released in the gaseous phase from the fuel forms P2O5(g) in primary reactions. The gaseous P2O5(g) may subsequently react with KOH(g) in secondary reactions to form KPO3(l, g). This compound reacts further through tertiary reactions and can incorporate solid Ca/Mg oxides in the structure. For biomasses with a high Ca content in the ash-forming elements, for example, bark, this general reaction pathway for the formation of phosphates with mixed cations may continue through substitution reactions where Ca replaces K in the phosphate structure. Generally, Ca phosphates are more stable than K phosphates, and if all the alkali is substituted for Ca through tertiary reactions, apatite is the final product.19 In Figure 1 this generalized reaction pathway is highlighted together with the composition of typical manures and co-combustion fuels.

The general reaction pathways for P in combustion are affected in terms of how the element is chemically associated in the biomasses and whether it is manure or residual streams from agriculture or forestry. The forms could be broadly classified as organically associated P, in dissolved salts, or mineralized materials (e.g., apatite).20 For poultry litter, P is present in the form of organically associated P (phosphate and phospholipid-type species) to a higher degree than that found in lignocellulosic biomass. The specific amount depends on the type of chicken; layer hen litter contains less organically associated P (average around 30%, up to 40−50%) compared to chicken litter (CL) (average around 50%, up to 75%).20 For other animal manures, the total P content is typically lower and to a larger extent associated with inorganic structures.20 This suggests that CL could be an attractive candidate for co-combustion with other residual streams from both agriculture and forestry to fully exploit the possibilities of incorporating more K in the phosphates formed during combustion.

The mixed cation phosphates that have been identified in ash fractions, for example, CaKPO4, K2MgP2O7, whitlockites, or even amorphous P compounds, may serve as fertilizer candidates or raw materials for further P recovery processes. In addition to these, amorphous Ca and K silicophosphates may form when combusting fuels rich in all four elements.21 Previously, the Na equivalent has been found in thermally treated sewage sludge ash,22 which has an increased water solubility compared to the untreated ash. To evaluate the leachability and plant availability of P in ash, ammonium citrate is preferably used,23 indicating mid- and long-term availability. NaOH−ethylenediaminetetraacetic acid (EDTA) and acidic oxalate were used in one study to evaluate the availability of P in biochars from swine manure, feedlot, and sewage sludge.24 It was concluded that the pyrophosphates were more easily extracted using NaOH−EDTA, whereas the Ca-rich orthophosphates required the stronger acidic oxalate. They also

Figure 1. Ternary composition diagram for alkali, alkali earth, and P components (as mass fraction, given in %). Fuels in this study and manure compositions from the Phyllis database are added to the diagram. The reaction pathway of P adapted from the study of Skoglund19 is highlighted: red indicates a gas−gas reaction, yellow a liquid−solid reaction, and blue a solid−solid reaction under combustion conditions.
concluded that chars produced at higher temperature contained higher amounts of orthophosphate.

Although the combustion of CL and other animal manure has been previously studied, the reaction pathways and chemical speciation of P in the formed ash have not been extensively investigated. A study on the pyrolysis of broiler litter by Uchimiya and Hiradate determined that P was found as orthophosphates at the highest pyrolysis temperature of 800 °C, but it is not certain whether this can be directly translated to combustion. The total amount of P in ash from the combustion of animal manure has also been evaluated, although the reaction pathways for P were not included. Elucidating on how ash transformation reactions of P in thermochemical processes are affected by the chemical speciation of P in manures, and their blends with K- and Ca-rich residual biomass fuels, can aid in selecting strategies on how to produce potentially valuable fertilizers in the ash fractions formed in the processes.

The aim of this work is, therefore, to determine the fate of P during fluidized bed co-combustion of CL with a K-rich agricultural residue [wheat straw (WS)] and a Ca-rich woody residue (bark). The effect of fuel blending on phosphate speciation in ash fractions will be studied, and the ash transformation reactions of P will be discussed.

2. MATERIALS AND METHODS

2.1. Fuel and Fuel Blends. The fuels used in the experiments were co-pelletized blends of CL with WS, bark (B), and pure CL (C100). Elemental ash analysis of fuels and fuel blends is presented in Table 1. Feedstock samples were transformed into ash according to DIN CEN/TS 14775. Initially, the samples were heated up to a temperature of 250 °C. This temperature was maintained for 60 min. Then, the temperature was increased to 550 °C and maintained until the transformation of the biomass into ash was completed. The ash produced from the feedstock was then subjected to X-ray fluorescence analysis using a PANalytical Axios Advanced analyzer (in a vacuum at 50 kV and 50 mA).

In Figure 1, CL, WS, and the bark and blends of the fuels have been plotted in a composition diagram for the CaO(+MgO)−K2O(−Na2O)−P2O5 system, together with other manures from the Phyllis2 database. The two fuels selected for blending with CL encompass a variation of both K and Ca and represent residual biomass fuels from agriculture and forestry. The blends were made as dry mass fractions with 70%/30% of WS/CL (CWS30) and 70%/30% of bark/CL (CB30). All fuels were pelleted to a size of 6 mm diameter to facilitate fuel feeding.

2.2. Combustion Experiments. The experiments were performed in a 5 kW bench-scale fluidized bed (Figure 2). The bed section has a 100 mm circular cross section and was operated with 540 g of bed material. The bed material used was natural K feldspar sand sieved to a size of 200–250 μm. Primary air was introduced at 50 Nl/min in the bottom through a stainless steel distribution plate, with 1% of the area perforated with 90 holes. Secondary air was introduced with an airflow of 30 Nl/min above the bed. The freeboard diameter is 200 mm and the total height of the apparatus is 2 m. The walls of the reactor were electrically heated to ensure the correct temperature. The experiments were performed with the aim of reaching 40 h of continuous fuel feed or until defluidization or ash overloading in the bed (blocking the fuel inlet) occurred. For C100 combustion, defluidization occurred after 11 h because of the high amounts of ash material in the bed; for CWS30 combustion, it occurred after 9 h (defluidization), and CB30 was combusted for the planned maximum duration of 40 h.

The bed temperature was maintained at 790–810 °C. The freeboard temperature was maintained at 800–820 °C. The flue gas composition was monitored using a Gasmet DX-4000 Fourier transform infrared spectroscopy analyzer. The experiments were carried out with slightly higher average O2 than the typical 8–10 vol % of O2, but the conditions were similar between experiments and allowed stable operation. No efforts were made to reduce NOx emissions by measures such as air staging, as the focus of this study is ash formation (Table 2). The exhaust gases passed through a cyclone with a cutoff diameter of 10 μm. To determine the particulate matter (PM) mass size distribution of the ash particles not trapped in the fly ash PM10 cyclone, particle sampling was carried out in the flue gas channel by using a 13-step low-pressure cascade impactor from Dekati Ltd. (DLPI), which classifies the size of ash particles according to the aerodynamic diameter in the range of 0.03–10 μm. Aluminum foils were used as substrates, and the impactor was heated to prevent water condensation during sampling. The 13 stages were further consolidated into fine (stage 1–7) and coarse (stage 8–13) fractions. Stages 1–7 consisted of submicron ash particles (<1 μm) and stages 8–13 contained particles in the size range of 1–10 μm. Bed and cyclone ash were collected for analysis after experiments when the reactor had reached near-room temperature.

2.3. Analysis. A Zeiss Evo LS-15 and JEOL JSM-IT300 were used for scanning electron microscopy (SEM) analysis in backscattered mode together with energy-dispersive X-ray spectrometry (EDS) to perform elemental analysis. The ash particles found in the bed and cyclone fractions were analyzed for both morphology and elemental composition through mapping, point, and area analyses. The analyses were made on both epoxy-encased particle cross sections and crushed particles mounted on carbon tapes. PM collected from the impactor was also analyzed for elemental composition. The stages 5 and 13, corresponding to the main peaks of fine and coarse modes of PM were analyzed. EDS analyses were made using a combination of elemental mapping, point, and area analyses. The elements included were K, Na, Ca, Mg, Fe, Al, Si, P, S, and Cl. The elements C and O were excluded as they are present in the epoxy resin and carbon tapes used for sample mounting.

The bed ash (including some bed material) and cyclone ash were subjected to powder X-ray diffraction (XRD) analysis using a PANalytical Empyrean diffractometer, employing Cu Kα radiation and a Pixel3D array detector. The samples were lightly crushed to a size of approx. 10 μm. Data collection was made with a rotating sample for a total acquisition time of 1 h for each sample. Data collection was performed at a 2θ between 10 and 70 with a scan interval of 0.007°. PANalytical HighScore Plus 4.831 together with ICDD PDF-4 database was used for the identification and quantification of the main crystalline phases. Quantification was performed with Rietveld analysis coupled with the K-factor method to estimate the amount of amorphous material. Pure crystalline Si was used as the external standard to correct the K-factor at the time of measurements.
3. RESULTS

3.1. Operational/Ash Formation. The amount of bed ash accumulated during the experiment was the deciding factor for the duration of each experiment because of its impact on operation. This was pronounced in the case of C100 where the experiments lasted 11 h prior to defluidization. This was caused by the amount of bed ash present in the system, which greatly influenced the bubbling bed properties. The blend with straw (CWS30) defluidized because of agglomerate formation after 9 h of operation. This is significantly longer than that observed for straw fuels combusted in the same bench-scale reactor previously.34,35 The defluidization was likely facilitated by the high bed ash-to-bed material ratio. In the case with CL and bark, the experiment was run continuously for the planned experimental period of 40 h.

3.2. Chemical Composition and Morphology of Ash Fractions. The chemical composition of the coarse and fine ash fractions, as determined by SEM−EDS, is shown in Figure 3. Comparing the bulk composition of bed ash and cyclone ash with the coarse PM fraction in the impactor stage 13 for all fuels, it is obvious that they are very similar within one fuel or fuel blend. This is consistent with the entrainment of bed ash particles, likely because of attrition. The similarity is attributed to the mechanics of the fluidized bed; all fractions represent the bed ash, and the size difference is due to the mechanical attrition of the ash. It should be noted that the bed ash also includes various amounts of the bed material, K-feldspar, whereas the cyclone ash contains a higher degree of ash. Analyses of the bed material, with a focus on the bed particle layer characteristics, can be found in the related papers,34,36 based on the same set of experiments.

All coarse ash fractions contained P-rich particles with different morphologies and elemental compositions, which will be further presented in the respective sections. For the purpose here, agglomerates are used to describe bed ash particles that contain different discrete regions of different compositions. These particle agglomerates may or may not be detrimental to operation, that is, cause bed agglomeration. Further, when the so-called melts are mentioned, this does not infer that the material was completely molten during operation. It rather places the focus on the mobility of elements in the particles. The exact state during operation could involve either solid-state diffusion, recrystallization in solids, or mobility of

Table 2. Flue Gas Composition during Steady-State Operation for Each Fuel Type

<table>
<thead>
<tr>
<th>fuel</th>
<th>( \text{H}_2\text{O} \text{ (vol %)} )^a</th>
<th>( \text{O}_2 \text{ (vol %)} )^b</th>
<th>( \text{CO}_2 \text{ (vol %)} )^b</th>
<th>NO ppm^c</th>
<th>NO\text{_}_2 ppm^c</th>
<th>N\text{_}2O ppm^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>7.6 ± 1.3</td>
<td>11.4 ± 1.4</td>
<td>14.4 ± 1.0</td>
<td>752 ± 594</td>
<td>34.5 ± 31.9</td>
<td>1.4 ± 6.6</td>
</tr>
<tr>
<td>CWS30</td>
<td>6.8 ± 1.9</td>
<td>11.6 ± 1.9</td>
<td>14.6 ± 1.2</td>
<td>235 ± 112</td>
<td>7.1 ± 5.9</td>
<td>2.9 ± 2.3</td>
</tr>
<tr>
<td>CB30</td>
<td>9.2 ± 1.6</td>
<td>11.3 ± 1.3</td>
<td>14.9 ± 1.1</td>
<td>173 ± 60</td>
<td>12.1 ± 7.0</td>
<td>0.5 ± 1</td>
</tr>
</tbody>
</table>

^aWet gas. ^bNormalized to dry gas. ^cNormalized to dry gas and 6 vol % \( \text{O}_2 \).
elements where only a small fraction of the material could be considered to exist in a liquid state. Such in situ observations are not possible and therefore based on appearance using SEM−EDS data.

For C100 and CB30, the P-rich bed ash particles typically contained K, Ca, Mg, P, and S. Their composition and appearance can be seen in Figures 3 and 4a,b, respectively. The smooth edges and presence of regions with homogeneous composition indicate that these particles were either partially or fully molten at some point during fuel conversion and they may therefore contain amorphous regions. Similar compositions were also found as outer layers on other particles, that is, on the bed material particles and other non-P-rich particles.

Unique for CWS30, two types of coarse ash particles were observed: one type mainly comprising K, Ca, Si, and P and another type dominated by K and Si. These particles were presumably partially or fully molten during operation, as evident by their shape and their composition reported in Figure 3. Similar to the case for C100 and CB30, these ash particles formed outer layers on other particles. Ash particles from CWS30 may contain P compounds precipitated from silicophosphate melts during cooling. This can be observed in Figure 4d, where small particles (lighter area) of about 1 μm are located evenly distributed individually and in clusters in a larger area of homogeneous composition (darker area). The presumably molten homogeneous area contains only small amounts of P (around 5 mol %), whereas these particles have a composition of about 15 mol % P, 30 mol % Si, 20 mol % Ca, and 20 mol % K on a C- and O-free basis, with minor amounts of Na, Al, Mg, and S.

Bed ash and cyclone ash from all experiments (C100, CWS30, and CB30) contained discrete particles with high concentrations of Ca or both Ca and Mg. Their size was typically 200−250 μm, but particles over 500 μm in size were also observed (Figure 4). These particles have a core consisting of alkali earth metals and an outer surface typically consisting of various combinations of K, Mg, P, and S.

P was not detected in the fine PM (<1 μm) by EDS analyses (Figure 3). Only equimolar proportions (50/50) of K, with small amounts of Na and Cl were detected for all fuels. For the coarse PM fractions (1−10 μm), the elemental composition reflects the bulk composition of bed and cyclone ashes, as shown in Figure 3. The only deviation was a lower Si content for coarse PM in CWS30 compared to its bed and cyclone ash. This could be caused by a stronger capture of Si in amorphous structures that accumulate to larger particles already in the bed, thereby avoiding entrainment in the flue gas.

3.3. XRD Analysis. The only P-containing compounds identified by XRD were hydroxyapatite and whitlockite, as presented in Table 3. This is consistent with the SEM−EDS finding, where Ca, P, and K are present in the same regions. Hydroxyapatite was identified as the only crystalline P compound for the C100 and CB30 bed ash fractions. As no crystalline phosphate was found in the CWS30 bed ash fraction and nearly half of the cyclone ash was estimated to be amorphous, P is likely present in amorphous parts of the bed ash as well. Whitlockite was observed in the C100 and CWS30 cyclone fractions. It is likely also present in the bed ash, diluted below the detection limit by the bed material.

The Ca compounds identified were CaO, Ca(OH)2, and CaCO3 for all fuels. Ca particles were most likely already included with the fuel, as Ca additives are common nutrient supplements for chicken feed.

4. DISCUSSION

4.1. Ash Composition. P was primarily found in the bed and cyclone ash fractions, as detected by SEM−EDS. Potentially volatile P appears to be captured in the crystalline and amorphous phases in the bed and coarse ash fractions. The XRD results show that P appears in hydroxyapatite in the bed ash particles of C100 and CB30, as well as all cyclone ashes. Whitlockite, Ca9MgK(PO4)7, was also identified in C100 and CWS30 cyclone ashes which suggests that the ash incorporates other cations than Ca in its orthophosphate structure. In addition to the crystalline compounds found, P appears in the amorphous structures as grains with discrete boundaries (Figure 4d). These grains may either have precipitated out of a melt or being dissolved into a melt.

A previous study has reported alkali−Ca−orthophosphate in addition to apatite and whitlockite in poultry litter ash, and it reports that the coarse ash is mainly dominated by crystalline alkali−Ca−phosphates. The study was also performed in a fluidized bed but at a lower bed temperature (655 °C average), although with a high freeboard temperature of about 930 °C.
In another study, CL ash was produced in a muffle furnace at 815 °C. Most of the crystalline P was found in apatite but also in minor amounts as KCaPO₄ and K₂CaP₂O₇. This is in contrast with the crystalline and amorphous structures found in the current work, where the co-combustion with WS yielded ash particles and outer layers with P likely present in amorphous structures. These structures, shown in Figure 4d, contain grains rich in K, Ca, P, and Si, which might be interesting for plant availability studies or P leaching.

The melts in bed ash from CWS30 have likely formed from molten K phosphates and K silicates as initial particles, subsequently incorporating Ca to form solids. Alternatively, molten K silicates dissolve Ca phosphates. The former is more likely because of the homogeneous composition around the grains and even distribution of these grains in the apparent melt. If it were a homogeneous silicophosphate melt with both P and Si oxides, the charge balance between the anions and cations suggests that Si exists as [SiO₃]²⁻ and P as [P₂O₇]⁴⁻ and the cations are shared between these. There are also K- and Si-rich ash particles, which probably acts as a step before the interaction with P-rich particles or gaseous P compounds.

Results from a thermodynamic equilibrium calculation with FactSage and GToxid database suggest an initial melt formation at 730 °C for the composition of the melt, but a dedicated investigation is required to verify this.

There are unreacted Ca- and Mg-rich particles that end up in the bed and cyclone ash for all fuel blends. They are too large to originate from oxalate particles known to exist in the bark, which could have been the case for CB30. Similar particles rich in Ca and Mg were reported by Bergfeldt et al., attributing them to dolomite present in CL. These particles might only react on the surface which leaves part of Ca unavailable for reaction with other ash-forming elements. This is especially important for interaction with ash that is expected to form sticky melts that can cover the Ca particle, rendering it unavailable for further reactions. This behavior that makes predictions of ash formation solely based on phase diagrams or thermodynamic equilibrium calculations is insufficient for these cases. This is relevant for all applications where Ca is used as an additive in combustion to remedy various problems.

The aluminosilicates orthoclase (KAlSi₃O₈) and leucite (KAlSi₂O₆) were also found in the bed ash fractions, most likely originating from the K feldspar bed material. In addition to these most common particles, all coarse ash fractions also showed examples of free and adhered particles containing alkali chlorides and sulfates. The occurrence of S in the P-rich particles is believed to originate from the reaction of alkali and alkali earth with gaseous S compounds on the surfaces. The Na

Figure 4. SEM backscatter images of typical bed ash particles in C100 [(a), top left], CB30 [(b), top right], and CWS30 [(c), bottom left] and zoom-in of the characteristics of typical molten areas found in bed samples from CWS30 [(d), bottom right]. Ca-rich particles can be seen in all cases. The rounded Ca–K–P–Mg–S-rich particles are highlighted in C100 and CB30. K–Ca–Si–P-rich particles/areas are highlighted for CWS30.

Table 3. Phases Identified Using XRD. Numbers Indicate Quantification in wt % of Phases from Rietveld Refinement Given as Intervals of 5 wt %

<table>
<thead>
<tr>
<th></th>
<th>C100</th>
<th>CB30</th>
<th>CWS30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bed ash</td>
<td>cyclone ash</td>
<td>bed ash</td>
</tr>
<tr>
<td>Ca₅(PO₄)OH</td>
<td>X 25–30</td>
<td>X 35–40</td>
<td>10–15</td>
</tr>
<tr>
<td>Ca₉MgK(PO₄)₇</td>
<td>15–20</td>
<td>15–20</td>
<td></td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>X 5–10</td>
<td>X 5–10</td>
<td></td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>&lt;5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAlSiO₃</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAlSi₂O₃</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>X</td>
<td>X</td>
<td>5–15</td>
</tr>
<tr>
<td>CaO</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>MgO</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>5–10</td>
<td>15–20</td>
<td>5–10</td>
</tr>
<tr>
<td>KCl</td>
<td>5–10</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Na₄K₂Cl</td>
<td>30</td>
<td>30</td>
<td>45</td>
</tr>
</tbody>
</table>

Only the cyclone ash fractions were quantified using XRD. Bed ash fractions had significant inclusions with varying amounts of bed material, which would greatly increase uncertainty in any quantification.

In another study, CL ash was produced in a muffle furnace at 815 °C. Most of the crystalline P was found in apatite but also in minor amounts as KCaPO₄ and K₂CaP₂O₇. This is in contrast with the crystalline and amorphous structures found in the current work, where the co-combustion with WS yielded ash particles and outer layers with P likely present in amorphous structures. These structures, shown in Figure 4d, contain grains rich in K, Ca, P, and Si, which might be interesting for plant availability studies or P leaching.

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The aluminosilicates orthoclase (KAlSi₃O₈) and leucite (KAlSi₂O₆) were also found in the bed ash fractions, most likely originating from the K feldspar bed material. In addition to these most common particles, all coarse ash fractions also showed examples of free and adhered particles containing alkali chlorides and sulfates. The occurrence of S in the P-rich particles is believed to originate from the reaction of alkali and alkali earth with gaseous S compounds on the surfaces. The Na
and K sulfates and chlorides identified by XRD confirm the observations from the elemental analysis with EDS.

4.2. Ash Transformation Reactions and Phosphate Speciation. The ash transformation reactions seem to generally follow a reaction pathway of primary, secondary, and tertiary reactions, where the interaction between K phosphates and Ca is dictated by Ca available for reaction. However, the full pathway for P discussed in the works by Boström et al. and Skoglund does not explain the apparent interaction between P and Si observed in these experiments. The interaction between K phosphates and K silicates is not described in the generalized reaction pathway shown in Figure 1. On the other hand, the suggested end product of whitlockite or apatite still seems to be valid. As Ca was included into the melt, these phases formed in the current work. In summary, the driving forces of the previously proposed reaction mechanism seem valid; it is the intermediate steps that have to be further evaluated regarding Si and P interaction. Dedicated studies have to be made on the amorphous particles assumed to be a homogeneous silicophosphate melt to determine if they can be formed by other P- and Si-rich fuel blends and how these melts interact with other bed materials. This is also important to understand in general as agricultural fuels rich in K and Si will potentially be combusted with other P-rich fuels.

There is still uncertainty whether the initial molten phase is K silicates or KPO₃, which subsequently dissolves the other and then further reacts toward thermodynamic equilibrium. The difference for CB30 and C100 in comparison to the particles in CWS30 is the lack of Si, meaning that the initial molten phase would probably have been molten KPO₃. Alternatively, the initial P anionic complex could potentially be [P₂O₇]⁴⁻, which is subsequently dissolved into a K-rich silicate melt. There is also some uncertainty as to why XRD analyses do not identify the composition of [P₂O₇]⁴⁻, as the findings from SEM—EDS analysis suggest. This is likely caused by a significant fraction of P that is still in the amorphous phase, as evident for the CWS30 ash particles.

4.3. Potential Use. If the ash is to be used as a fertilizer, the whitlockite-bearing materials (C100 and CWS30) are more interesting compared to the hydroxyapatite-rich CB30, as whitlockite has previously been identified and attributed promising results in plant growth experiments. P in amorphous particles might also be interesting for plant growth; it should be investigated if it is in an available form. Plant growth studies with such ash fractions should be further complemented by the studies on emissions from suitable fuel blends with manure. With such information, it would be feasible to evaluate whether the inclusion of excess manures such as CL in the bioenergy sector is both environmentally and technoeconomically sound.

5. CONCLUSIONS

In all experiments, fuel P was only detected in the coarse ash fractions, that is, the bed ash particles, cyclone ash, and coarse PM (>1 μm); no P could be detected in the fine PM (<1 μm). SEM—EDS showed that P was mainly present in ash particles rich in K–Ca–P-rich amorphous structures (possibly as melts), for pure CL, and the blend with 30% CL in bark. For the 30% CL–WS blend, P was mainly found in a K–P–Si-rich amorphous structure, that is, potentially in a silicophosphate melt. P in crystalline compounds was identified in apatite and whitlockite for pure CL and WS blend. Bark blends produced ash with P located in apatite. From a plant availability point of view, co-combustion of CL and WS is therefore an interesting route.

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Notes
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