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Release and Transformation of Inorganic Elements in Combustion of a High-Phosphorus Fuel

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 Supporting Information

ABSTRACT: The release and transformation of inorganic elements during grate-firing of bran was studied via experiments in a laboratory-scale reactor, analysis of fly ash from a grate-fired plant, and equilibrium modeling. It was found that K, P, S, and to a lesser extent Cl and Na were released to the gas phase during bran combustion. Laboratory-scale experiments showed that S was almost fully vaporized during pyrolysis below 700 °C. Sixty to seventy percent of the K and P in bran was released during combustion, in the temperature range 900–1100 °C. The release of K and P was presumably attributed to the vaporization of KPO_3 generated from thermal decomposition of inositol phosphates, which were considered to be a major source of P and K in bran. The influence of additives such as CaCO_3 , $\text{Ca}(\text{OH})_2$, and kaolinite on the release was also investigated. Ca-based additives generally increased the molar ratio of the released K/P, whereas kaolinite showed an opposite effect. Thermodynamic modeling indicated that the fly ash chemistry was sensitive to the molar ratio of the released K/P. When the molar ratio of the released K/P was below 1, KPO_3 and $\text{P}_4\text{O}_{10}(\text{g})$ were the main stable K and P species at temperatures higher than 500 °C. Below 500 °C, the KPO_3 and $\text{P}_4\text{O}_{10}(\text{g})$ may be converted to $\text{H}_3\text{PO}_4(\text{l})$, which may cause severe deposit build-up in the economizers of a grate-fired boiler. By increasing the molar ratio of the released K/P to above 2, the equilibrium distribution of the K and P species was significantly changed and the formation of $\text{H}_3\text{PO}_4(\text{l})$ was not predicted by thermodynamic modeling.

1. INTRODUCTION

Utilization of biomass and biomass-derived waste materials in heat and power production plants is an important approach to reduce fossil fuel consumption and thereby the CO_2 level in the atmosphere. Seed-originated biofuels constitute a special type of biofuel which is usually characterized by a significantly higher P content than other biofuels.^{1–7} Typical examples are grain from wheat, oat, or other biomass,^{3,4,7} bran from wheat or rice,⁸ and rapeseed meal/cake, which is a residue from rapeseed methyl ester (biodiesel) production.^{1,5,9,10} In northern European countries, utilization of P-rich biofuels in grate-fired or fluidized bed combustion systems has gained interest in recent years.^{1,2,4,5,9–11} The main driving force is the target of achieving a 20% renewable energy share in the EU by the year of 2020,¹² and the potential economical benefits from the possible low price of these biofuels.^{1,2}

Combustion of high-P biofuels may induce ash related problems in boilers, such as bed agglomeration,⁵ slagging,^{3,5} fouling,⁵ corrosion,² fine particle emission,⁴ and deactivation of the SCR units.^{13,14} These problems are linked to the high P and K content in these biofuels.^{1–5} During combustion, part of the P and K is released and involve in complicated gas–gas and/or gas–solid reactions with other ash forming elements such as S, Cl, Ca, Mg, Si, and Al. These transformations may generate K-phosphates with low melting temperature (such as KPO_3) and lead to bed agglomeration, slagging, and fouling problems.^{3,5} On the other hand, some phosphorus compounds (such as Ca-phosphates) may mitigate ash deposition and corrosion in boilers, by forming ash species with

high melting temperature and by converting the alkali chlorides to alkali-calcium phosphates and $\text{HCl}(\text{g})$.¹⁵ To better understand and minimize the ash related problems occurring during combustion of P-rich biofuels, a systematic study on the ash release and transformation mechanisms related to these fuels was conducted.

The aim of the present work was to characterize the release and transformation of inorganic elements during grate-firing of a residual bran from bioethanol production. This was achieved by multiple approaches. The association of P and other inorganic elements in bran was assessed through a literature review and SEM-EDS (scanning electron microscopy and electron dispersive X-rays spectroscopy) analysis. The release of inorganic elements was studied by conducting experiments in a horizontal tube reactor and by comparing with full-scale data obtained from a grate-fired plant. In addition to pure bran combustion, the effect of different additives such as CaCO_3 , $\text{Ca}(\text{OH})_2$, kaolinite, and MgCO_3 was also investigated. To interpret the observed release behavior, the bran ash and a typical phosphorus compound, which might appear in ash, were characterized by an STA (simultaneous thermal analyzer) and by high-temperature oven experiments. The transformation of the vaporized inorganic elements at different release conditions was investigated by thermodynamic modeling.

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Table 1. Chemical Composition of the Bran

properties	bran	properties	bran
moisture (wt %)	8.22	P (wt % dry)	1.1
ash (wt % dry)	5.3	Si (wt % dry)	0.13
C (wt % dry)	45	Mg (wt % dry)	0.38
H (wt % dry)	6.3	Ca (wt % dry)	0.092
O (wt % dry)	42.75	Al (wt % dry)	0.008
N (wt % dry)	2.65	Fe (wt % dry)	0.021
S (wt % dry)	0.19	Ti (wt % dry)	
Cl (wt % dry)	0.071	Mn (wt % dry)	
K (wt % dry)	1.3	Na (wt % dry)	0.005

2. EXPERIMENTAL SECTION

2.1. Fuel Characterization. Residual bran from bioethanol production is used as the fuel in a grate-fired plant in a European country. The chemical composition of the bran was analyzed by ICP-OES (inductively coupled plasma-optical emission spectroscopy). As shown in Table 1, K, P, and Mg are the dominant inorganic elements. The P content is significantly higher than of other biofuels such as straw¹⁶ and wood⁵ but is comparable with that of P-rich biofuels such as rapeseed cake⁵ and oat grain.⁴ The molar ratio of K/P in the bran is 0.94, which is within the range (~0.8–1.0) reported for other P-rich biofuels.^{3–5,10} Other important inorganic elements in the bran are S, Si, Ca, and Cl. The N content in the bran is about 2.2 wt %, which is much larger than that of other biofuels such as straw¹⁶ and wood,⁵ probably due to the high protein content in the seed of biomass.¹⁷ The particle size distribution of the bran was characterized by a laser diffraction method (Malvern Mastersizer 2000 particle size analyzer), showing that the d_{50} (meaning that 50 vol % of the particle are below this size) of the bran is about 230 μm .

2.2. Additives. Additives were used in the experiments to study their influence on the release of inorganic elements during bran combustion. The applied additives were CaCO_3 , $\text{Ca}(\text{OH})_2$, kaolinite, and MgCO_3 . The CaCO_3 had a purity above 97% and particle size below 125 μm . The $\text{Ca}(\text{OH})_2$ and MgCO_3 were powdery pure compounds. The d_{50} of the $\text{Ca}(\text{OH})_2$ particles was about 3 μm , and all of the particles were below 60 μm . The kaolinite was also a powdery pure compound, with measured d_{50} about 8 μm .

2.3. Laboratory-Scale Release Experiments. Experiments were carried out in a horizontal tube reactor. The release was quantified by a mass balance calculation based on weight measurement and chemical analysis of the raw fuel and residual ash from the experiment. The details regarding the experimental setup and mass balance calculation can be found elsewhere.^{18,19}

During the experiment, the tube reactor was preheated to a desired temperature. A platinum/alumina boat with 5–10 g sample was then inserted in the reactor. A primary gas (5 NL/min, 100% N_2) was added to create a pyrolyzing condition for the sample, and downstream a secondary gas (5 NL/min, 20% O_2) was injected to combust the volatiles released during pyrolysis. This pyrolyzing condition was created to simulate the combustion in a grate-fired system, where the devolatilization and char oxidation may primarily take place in different zones. In addition, it can also minimize the temperature overshoot that may be caused by volatile oxidation. After the sample was placed at pyrolyzing condition for 60 min, 1% of O_2 was introduced to the primary gas, and the O_2 content in the primary gas was increased stepwise to 20% to minimize the temperature overshoot during char combustion.¹⁸ The maximum temperature overshoot was measured to be 50 $^\circ\text{C}$ during the experiments, by inserting a thermocouple into the fuel bed. After a total experimental period of 200 min, the boat was removed from the reactor and cooled to room temperature in a N_2 environment. The weight of the residual ash was measured and the chemical composition was analyzed by ICP-OES. For

the experiments carried out at pyrolyzing condition, the primary gas was maintained as N_2 during a total experimental duration of 180 min. The combustion/pyrolysis experiments at different conditions were repeated several times, and the reproducibility was found to be satisfactory by comparing the quantity of residual ash/char.

The experimental matrix is shown in Table 2. The combustion and pyrolysis experiments of pure bran were carried out at temperatures from 300 to 1100 $^\circ\text{C}$. The effect of different additives (CaCO_3 , $\text{Ca}(\text{OH})_2$, kaolinite, and MgCO_3) on the release of inorganic elements during bran combustion was studied at 1100 $^\circ\text{C}$. During the additive experiments, the bran was well-mixed with the additive in a mortar. The properties of the bran and additives were described previously. For comparison, some molar ratios of the inorganic elements in the fuel mixture were calculated and listed in Table 2.

2.4. Full-Scale Tests. The bran used in the present work was obtained from a full-scale plant, where it was combusted on a grate. The hot flue gas from the boiler chamber subsequently passed through the superheaters and economizers to produce heat and power. Downstream of the economizers, baghouse filters were installed to remove the fly ash particles from flue gas. To reduce the emissions of SO_2 and HCl, NaHCO_3 particles were injected before the baghouse filters.

The plant was initially operated with pure bran. However, after successful operation of a few months, the baghouse filters were found to be blocked by “sintered” fly ash, which could not be removed by pressurized air and hindered the continuous operation of the plant. In addition, severe ash deposition was observed in the economizers of the plant, with flue gas temperatures of ~380–180 $^\circ\text{C}$. To minimize these problems, the plant was operated with the addition of 5–8 wt % CaCO_3 . It appeared that the baghouse filter problem was mitigated by addition of CaCO_3 and by changing the operational condition of the filter, whereas the ash deposition problem in the economizers still appeared occasionally.

A large number of fly ash samples were collected from the plant and the composition of these were analyzed by SEM-EDS. The fly ash samples were collected during an operation period of more than a year, both with and without CaCO_3 addition. It should be noted that the composition of the bran used on the grate-fired plant varied over time, and often deviated from that shown in Table 1. In addition, the CaCO_3 applied in the plant was also different from that described in section 2.2. Due to these factors, the full-scale results can only be compared with the results from laboratory-scale experiments qualitatively.

2.5. Characterization of the Ash/Compound Thermal Behavior. A simultaneous thermal analyzer (STA, Netzsch 449 F1) was applied to study the thermal behavior of KH_2PO_4 , which is considered to be a P and K containing compound that may be formed during bran combustion. The STA was operated at 5% O_2 in N_2 . During the test, approximately 5 mg of the KH_2PO_4 was placed in a Pt–Rh crucible, and the crucible was heated from 25 to 1400 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$. Both the TG (thermogravimetric) and DSC (differential scanning calorimetry) curves were obtained from the STA analysis. The TG curve shows the continuous sample mass loss during heat-up, whereas the DSC curve gives a continuous measurement of the heat flow in the sample as a function of temperature.

A mixture of CaCO_3 and bran ash produced in the horizontal tube reactor at 700 $^\circ\text{C}$ was also tested in the STA. The Ca/P molar ratio in the mixture was controlled to be 1.68, similar to the condition of experiments 10 and 11 in Table 2. The STA was operated at 5% O_2 . During the test, the mixture was heated from 25 to 1100 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$, and then kept at 1100 $^\circ\text{C}$ for 6 h. To study the possible interactions between the bran ash and CaCO_3 , the experimental weight loss of the mixture was compared with the weight loss calculated from the pure components tested at the same conditions.

Furthermore, a high temperature oven was applied to study the reactions between KH_2PO_4 and $\text{Ca}(\text{OH})_2$. During the test, KH_2PO_4 and $\text{Ca}(\text{OH})_2$ were mixed in a molar ratio of 1:1, and the mixture was

Table 2. Experimental Matrix of the Release Experiments in the Horizontal Tube Reactor

experiment no.	sample	experiment condition	temp (°C)	molar ratio in the fuel				
				K/P	Ca/P	Mg/P	K/Si	K/(Cl+2S)
1	bran	pyrolysis	300	0.94	0.06	0.45	7.18	2.4
2	bran	pyrolysis	500	0.94	0.06	0.45	7.18	2.4
3	bran	pyrolysis	700	0.94	0.06	0.45	7.18	2.4
4	bran	pyrolysis	900	0.94	0.06	0.45	7.18	2.4
5	bran	combustion	500	0.94	0.06	0.45	7.18	2.4
6	bran	combustion	700	0.94	0.06	0.45	7.18	2.4
7 ^a	bran	combustion	900	0.94	0.06	0.45	7.18	2.4
8	bran	combustion	1100	0.94	0.06	0.45	7.18	2.4
9	Bran+2 wt %CaCO ₃	combustion	1100	0.94	0.69	0.45	7.18	2.4
10	bran + 5 wt % CaCO ₃	combustion	1100	0.94	1.68	0.45	7.18	2.4
11	bran + 3.75 wt % Ca(OH) ₂	combustion	1100	0.94	1.67	0.45	7.18	2.4
12	bran + 5 wt % kaolinite	combustion	1100	0.99	0.07	0.46	0.69	2.53
13	bran + 3.18 wt % MgCO ₃	combustion	1100	0.94	0.06	1.56	7.18	2.4

^a Chemical analysis has not been performed as the residue ash cannot be totally removed from the boat.

heated from room temperature to 1500 °C at a rate of 10 °C/min. To identify the possible reactions between KH₂PO₄ and Ca(OH)₂, the obtained mass loss of the mixture was compared with that estimated from the pure compounds.

3. RESULTS AND DISCUSSION

3.1. Release of Inorganic Elements in Bran Combustion. *3.1.1. Association of Inorganic Elements in High-Phosphorus Biofuels.* To evaluate the association of inorganic elements in biofuels, a widely used approach is the chemical fractionation method, which was originally developed for coal²⁰ and further modified for biomass.²¹ In the chemical fractionation method, the fuel is leached subsequently in different solutions (water, 1 M ammonium acetate, and 1 M hydrochloric acid), and the ash forming elements in the solutions as well as in the residue are analyzed to quantify the associations of these elements.^{21,22} This method has been applied to study the association of inorganic elements in a rapeseed cake,⁵ which is a typical high-P biofuel. It revealed that approximately 70% of the P in the rapeseed cake was water/ammonium acetate soluble, whereas the remaining P was HCl soluble. For K, the water/ammonium acetate soluble comprised more than 90% of the total K in the fuel. Similar tendencies were also seen for Cl, Na, and Mg, indicating that the majority of P, K, Cl, Na, and Mg in the rapeseed cake may exist as water-soluble and/or organically bounded elements. For S, a certain fraction (~30%) was found to be present in the solid residue. This fraction of S might be covalently bonded to the organic structure of the fuel, and might be released to gas phase during combustion.^{5,9} The majority of Ca in the rapeseed cake was ammonium acetate/HCl soluble, implying that the Ca might be associated with carboxylic groups or exist as calcium oxalate (CaC₂O₄).⁵

Apart from the chemical fractionation method, the association of P in seed-originated biomass such as rapeseed meal, grains, and bran has been investigated extensively in biological studies.^{17,23–27} These studies generally suggest that the majority of P in seed-originated biomass is present as phytic acid (see the chemical structure in Figure 1) or phytate if the phytic acid is combined with inorganic elements such as K, Mg, and Ca. It was

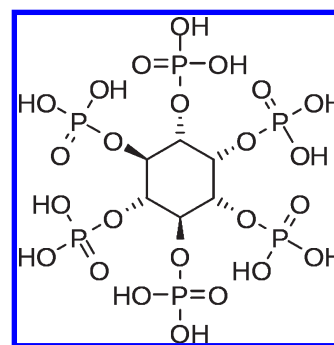


Figure 1. Chemical structure of phytic acid (also known as inositol hexakiphosphate or Ins P6).

reported that phytic acid/phytate represented approximately 75 ± 10% of the total P in a seed, and the contribution could be greater than 90% in a mature seed.²⁷ An investigation carried out on a buckwheat bran showed that 60–92% of the total P in the bran was present as phytic acid/phytate.¹⁷ For a rapeseed meal, it was reported that about 69% of the total P in the biomass was present as inositol phosphates, and the phytic acid/phytate composed of 64% of the inositol phosphates.²³ Phytic acid is a strong chelating agent that can form complexes with mineral cations such as K, Mg, Ca, and Zn,^{17,28} and the formed phytate is the major storage of P, K, and Mg in seeds.¹⁷ Minerals that are associated as phytate are normally rather stable and poorly soluble at the pH of gastrointestinal tract.²⁵ The thermal stabilities of some solid state complexes of phytic acid with Mn, Co, Ni, Cu, Zn, and Sn were investigated in a thermogravimetric analyzer (TGA).²⁸ When the complexes were heated in air to 900 °C, the main thermal decomposition steps were found to be the loss of moisture, the decomposition of the aliphatic ring, and the loss of C₆H₆ due to combustion. The P in the complexes was not released during the thermal decomposition up to 900 °C, due to the formation of stable phosphates.²⁸

For the residue bran used in the present work, SEM-EDS analysis has been performed on the fuel to evaluate the association of inorganic elements. A typical result is shown in Figure 2, together with spot-analysis compositions. The result is considered

to be representative for a number of SEM-EDS analyses performed. It is seen that some spherical particles with heavier elements (illustrated by the brighter color) are present in the bran. The size of these spherical particles is around 1–3 μm , and EDS analysis of the particles (see spectra 1 and 3 in Figure 2) implies that the P, Mg, and K content in these particles is significantly higher than that in other parts of bran. The results are generally consistent with the observations in literature,^{26,29} where the phytate in wheat bran or other mature grains was found to be concentrated in the electron-dense parts of the protein storage vacuoles called phytate globoids, which had a size up to 5 μm . The P, Mg, and K content in the globoids was reported to be 5–7 times higher than that in the whole bran, suggesting that the globoids are a major source of P, Mg, and K in bran.²⁹

According to the literature results and the SEM-EDS analysis, it is conceivable that the majority of P, Mg, and K in the bran used in this work are present as phytic acid/phytate or other inositol phosphate, which are concentrated in globoids. When bran is combusted at high temperature, the P in phytic acid/phytate may

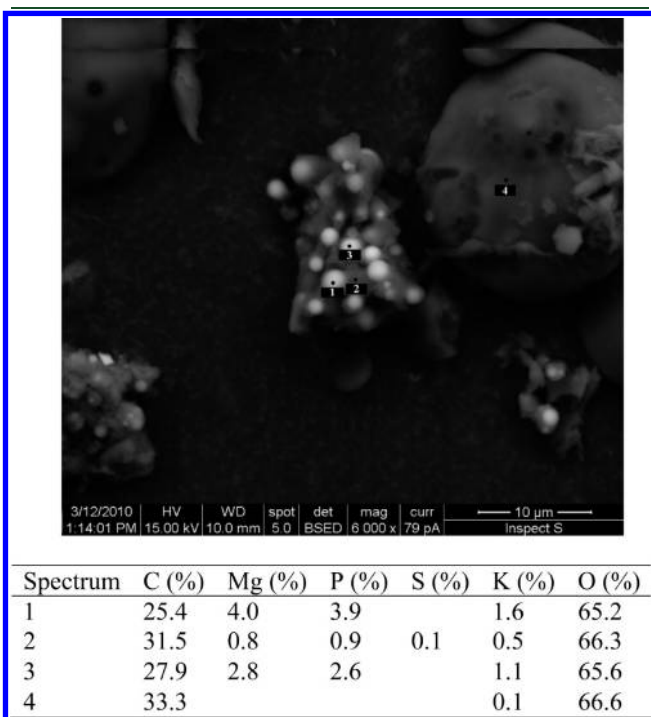


Figure 2. Back scatter electron image of the bran, with spot analysis compositions (molar percentage).

be transformed to phosphorus oxides/phosphates; thus the vaporization of P, Mg, and K in combustion may to a large extent depend on the vapor pressure of the phosphorus oxide/phosphates. A detailed analysis of the associations of P and other inorganic elements in bran can be performed through similar approaches, as used extensively in biological studies.^{17,23–27} However, it is outside the scope of this work.

3.1.2. Release in Laboratory-Scale Experiments. Figure 3a shows the release of P, K, Mg, and S during bran pyrolysis at different temperatures. It can be seen that the release of P, K, and Mg is negligible up to 900 $^{\circ}\text{C}$, implying that these elements in bran are not associated with the volatiles released during pyrolysis. This also indicates that the inorganically associated or char bounded P, K, and Mg are rather stable up to 900 $^{\circ}\text{C}$. A similar study on wheat straw showed that the release of K was approximately 20% at a pyrolysis temperature of 900 $^{\circ}\text{C}$ and a pyrolysis duration of 120 min.³⁰ The release of K during straw pyrolysis was attributed to the vaporization of KCl present in the pores of char matrix, and the process was considered to be affected by pyrolysis duration.³⁰ In our experiments, pyrolysis duration at 900 $^{\circ}\text{C}$ was 180 min, and vaporization of K was still not observed. This suggests that the presence and vaporization of KCl during bran combustion are negligible, in agreement with the low Cl content of the bran. Compared to that of P, K, and Mg, the behavior of S is quite different. More than 95% of the S is released to gas phase during bran pyrolysis at 500 $^{\circ}\text{C}$. A similar phenomenon has been seen during straw pyrolysis at 500 $^{\circ}\text{C}$, although the percentage of the released S was smaller ($\sim 40\%$).³⁰ The significant release of S below 500 $^{\circ}\text{C}$ suggests that the majority of S in bran is organically associated and is released together the volatiles.

Figure 3b depicts the release of P, K, Mg, and S during bran combustion at 500, 700, and 1100 $^{\circ}\text{C}$. The results of the experiment at 900 $^{\circ}\text{C}$ are not shown, because the residual ash from this experiment is molten and cannot be fully removed from the boat. From Figure 3b, it can be seen that the release of P, K, and Mg is negligible at combustion temperatures of 500 and 700 $^{\circ}\text{C}$, whereas the release of S is almost complete, in agreement with the pyrolysis results. The data suggest that during char combustion, organically associated P, K, and Mg in the bran are likely transformed to stable inorganic compounds that are not vaporized at 700 $^{\circ}\text{C}$. For the experiment at 900 $^{\circ}\text{C}$, although the release of P, K, and Mg is not quantified, the ash amount from the experiment indicates that the vaporization of inorganic elements is not significantly greater than that of 700 $^{\circ}\text{C}$.

When the combustion temperature is increased from 900 to 1100 $^{\circ}\text{C}$, a significant decrease in residual ash amount is observed (Figure 3b), implying that a large fraction of the inorganic elements

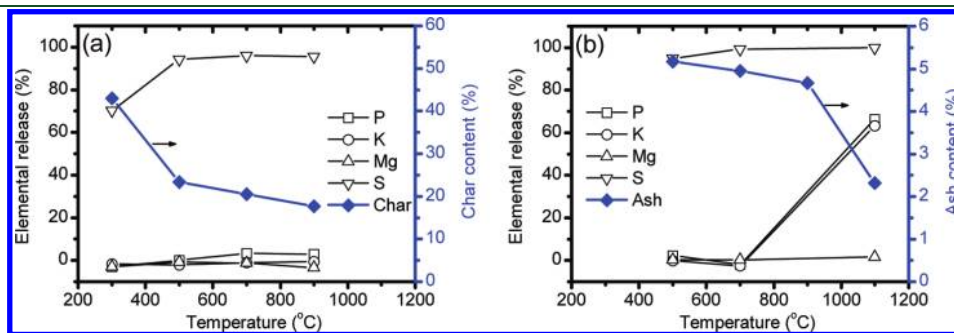


Figure 3. (a) Release of P, K, Mg, and S, and the char content of bran at different temperature during pyrolysis. (b) Release of P, K, Mg, and S, and the ash content of bran at different temperature during combustion.

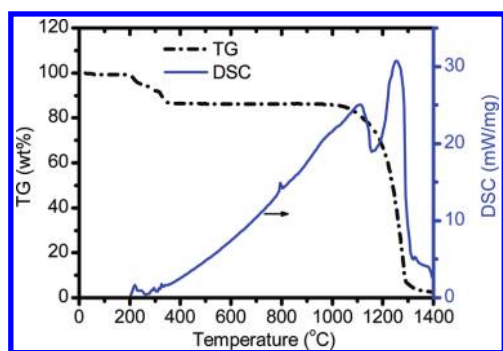


Figure 4. STA (simultaneous thermal analysis) measurement of pure KH_2PO_4 at 5% O_2 condition and heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

is released in this temperature range. This is consistent with the significant release of K and P obtained at $1100\text{ }^\circ\text{C}$, which is about 63% and 66%, respectively. The release of Mg is still negligible at $1100\text{ }^\circ\text{C}$, whereas the release of S is almost 100%. The results suggest that the major ash forming elements that are vaporized during bran combustion are K, P, and S. In addition, it should be mentioned that the Na and Cl content in the residual ash from the $1100\text{ }^\circ\text{C}$ experiment is below the detection limit of ICP-OES (i.e., $\text{Na} < 0.02\text{ wt } \%$ and $\text{Cl} < 0.05\text{ wt } \%$). This indicates that the majority (>90%) of the Na and Cl in the bran are released to the gas phase at $1100\text{ }^\circ\text{C}$. In addition to the elements shown in Figure 3, the release of other inorganic elements, such as Si and Ca, is generally found to be negligible during bran combustion. The reliability of the experiments can be reflected by the results of Mg, which should be a nonvolatile element at the given experimental conditions. As shown in Figure 3, the maximum deviation of Mg release from the baseline (0%) is about 3%, which indicates a good reliability of the experiments.

The release of K, Mg, and P during bran pyrolysis may be explained by the association of these elements. The majority of K, Mg, and P in bran may be present as phytate/phytic acid or other inositol phosphates, as discussed in the previous section. During bran pyrolysis, the structure of the inositol phosphates may not decompose and the vaporization of K and P may not occur. On the other hand, the decomposition of inositol phosphates may have happened at pyrolysis temperature of $900\text{ }^\circ\text{C}$, but the temperature is not high enough to vaporize the K and P species. Thus the release of K and P is negligible at pyrolysis temperature of $900\text{ }^\circ\text{C}$.

During bran combustion, it is likely that the K, Mg, and P present as phytate/phytic acid (or other inositol phosphates) are converted to K-phosphate, Mg-phosphate, K-Mg-phosphate, or phosphorus oxide. According to the structure of phytic acid shown in Figure 1, a major K-phosphate product from the combustion of inositol phosphates is conceivably KPO_3 . The thermal behavior of KPO_3 at high temperature has been evaluated in a STA instrument by heating a pure KH_2PO_4 sample from 25 to $1400\text{ }^\circ\text{C}$. KH_2PO_4 decomposes to KPO_3 at temperatures below $400\text{ }^\circ\text{C}$.^{31,32} This transformation is confirmed by the STA results presented in Figure 4, showing that the mass loss of KH_2PO_4 is about 13.7 wt % at $400\text{ }^\circ\text{C}$. When the KPO_3 formed is heated further, a DSC peak appears at around $800\text{ }^\circ\text{C}$, accompanied by a negligible mass loss. This DSC peak suggests that an endothermic process (melting) occurs at around $800\text{ }^\circ\text{C}$, in agreement with the melting point of KPO_3 ($807\text{ }^\circ\text{C}$) reported in literature.³³ It should be noted that the KPO_3 formed in the STA experiment is probably

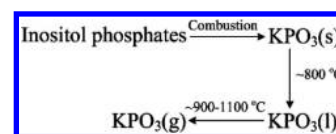


Figure 5. Proposed primary release mechanism of P and K during bran combustion.

present in a polymer form, as suggested in the literature.^{31,32} Thus the observed melting temperature is related to the chain length of the polymer, which is not determined in the present work. According to the TG curve, the vaporization of KPO_3 starts at around $1000\text{ }^\circ\text{C}$ and is almost completed at around $1300\text{ }^\circ\text{C}$. Although the vaporization degree of the KPO_3 seems to be not significant at $1100\text{ }^\circ\text{C}$, one should be aware that the STA is operated at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$; thus it may be difficult to achieve equilibrium in such a heating rate. With a longer holding time at $1100\text{ }^\circ\text{C}$, the KPO_3 may be fully vaporized.

According to the results shown above, the primary release mechanism of P and K during bran combustion is proposed in Figure 5. During combustion, the inositol phosphates in bran may be converted to KPO_3 . At temperatures around $800\text{ }^\circ\text{C}$, the KPO_3 may be melted. When the temperature is increased to $900\text{--}1100\text{ }^\circ\text{C}$, vaporization of KPO_3 may happen, which may release P and K to the gas phase. This proposed mechanism is supported by several experimental observations. First, the residual ash from bran combustion is melted in the temperature range $700\text{--}900\text{ }^\circ\text{C}$, which is consistent with the melting temperature of KPO_3 . However, the initial melting temperature of the residue ash may not be determined by the melting point of pure KPO_3 , but rather by the closest eutectic or peritectic point in the $\text{K}_2\text{O-MgO(CaO)-P}_2\text{O}_5$ system.³ Second, the release of K and P during bran combustion happens in the temperature range $900\text{--}1100\text{ }^\circ\text{C}$, which is also in agreement with the observed vaporization behavior of KPO_3 . Moreover, during bran combustion at $1100\text{ }^\circ\text{C}$, the molar ratio of the released K/P is about 0.9, which further supports that KPO_3 is likely a major K and P species vaporized. However, the molar ratio of the released K/P also indicates that a small fraction of P may be released in other forms. Because the release of Na is found to be significant ($\sim 90\%$) in the temperature range $900\text{--}1100\text{ }^\circ\text{C}$, it is likely that Na-phosphate is formed and released during bran combustion. The release of P as oxides or phosphoric acids is less likely to happen, because the majority of phosphorus oxides or phosphoric acids have high vapor pressures at $700\text{ }^\circ\text{C}$,³⁴ which contrasts with the negligible P release observed during bran combustion at $700\text{ }^\circ\text{C}$. For the retention of P and K in residual ash at $1100\text{ }^\circ\text{C}$, it is probably related to the formation of Mg-K or Ca-K phosphates, which can have melting points higher than $1100\text{ }^\circ\text{C}$.³³ For K, K-silicates or K-aluminosilicates may also be a source of the K found in residual ash at $1100\text{ }^\circ\text{C}$.

It should be noted that the mechanism of K and P release proposed above requires further confirmation through analysis of the properties of the residual ash from bran combustion (such as XRD, SEM-EDS, or chemical fractionation analysis) as well as sampling the released K and P species and performing XRD or wet-chemical analysis. These investigations are beyond the scope of this work and are subjected to future work.

3.1.3. Release in Full-Scale Grate-Fired Plant. To compare the release results obtained from the laboratory-scale experiments with those of full-scale plant, the typical morphology and composition of the fly ash particles collected in the baghouse filter of the

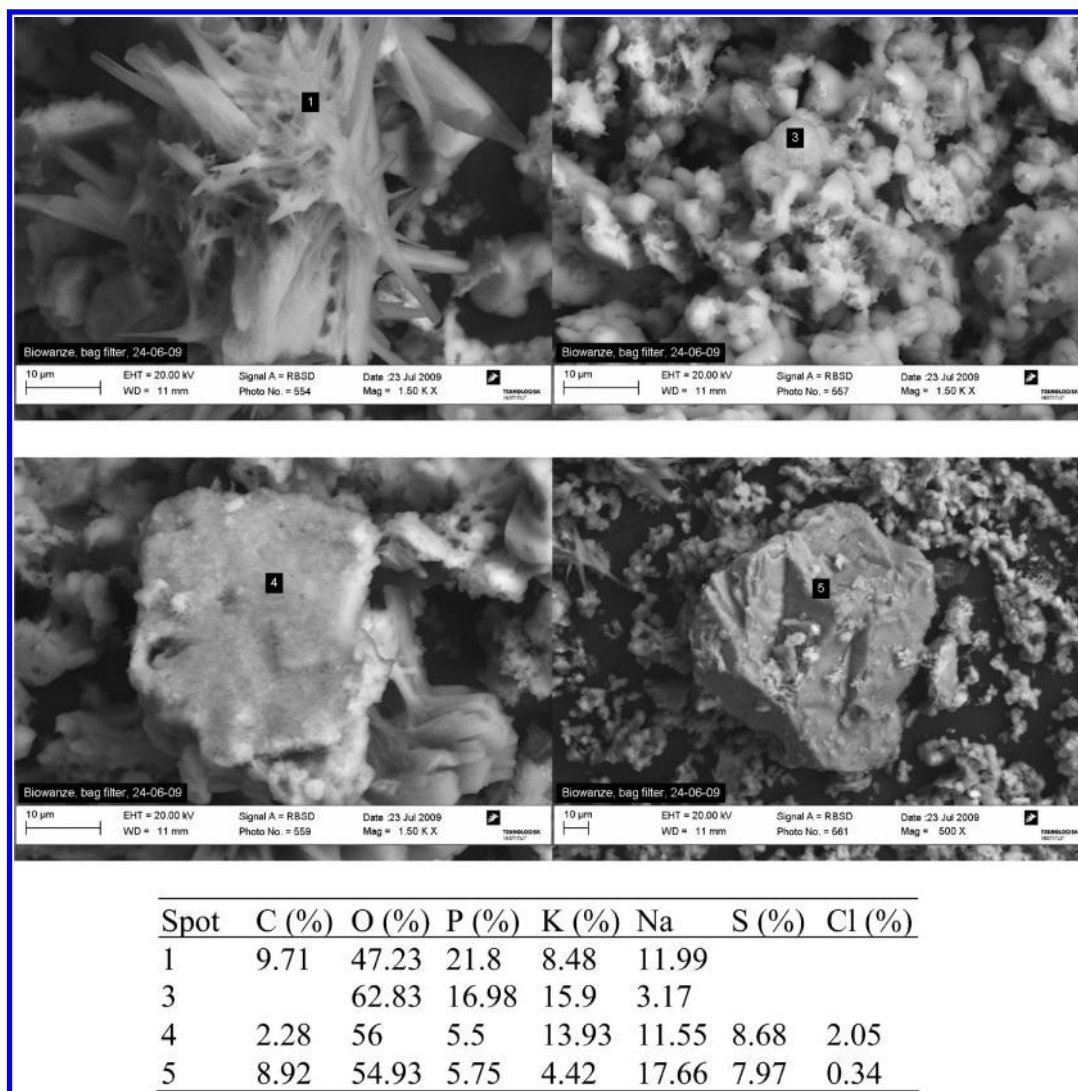


Figure 6. Typical morphology of the fly ash collected during pure bran combustion in the grate-fired plant, with the spot compositions (molar percentage).

grate-fired plant was investigated by SEM-EDS and presented in Figure 6. Because the fly ash from a grate-fired system is dominated by vaporized inorganic species,^{35,36} the composition can provide an estimation of the release of inorganic elements during bran combustion. From Figure 6, it can be seen that the fly ash primarily consists of P, K, Na, and S. The presence of Cl is observed in some particles, but in smaller amounts compared to other inorganic elements. The P and K in the filter ash are probably a result of the vaporization of P and K during bran combustion. However, the majority of Na in the collected fly ash probably originates from the NaHCO_3 particles injected in front of the baghouse filters, as the Na content in bran is usually quite low. In addition, because the purpose of NaHCO_3 injection is to reduce the SO_2 and HCl emission from the plant, it naturally causes an increase of the S and Cl content in fly ash. In addition to SEM-EDS analysis, XRD analysis on the fly ash shows that the major crystalline phases are KH_2PO_4 and $\text{K}_3\text{Na}(\text{SO}_4)_2$.

Besides the typical fly ash composition, the bulk composition of a number of fly ash samples collected from the plant was analyzed by SEM-EDS. It is generally found that the molar ratio of K/P in fly ash was in the range 0.9–1.2, when the plant was

operated with pure bran. This is comparable with the molar ratio of the released K/P (~ 0.9) obtained in the laboratory-scale experiment at 1100°C . The molar ratio of the released K/S in the laboratory-scale experiment at 1100°C is around 3.5, which is also in agreement with the range (~ 3 – 4.5) found in the fly ash from the grate-fired plant. This suggests that the results obtained from the laboratory-scale experiment at 1100°C are representative, at least qualitatively, for the release of inorganic elements in the grate-fired plant.

3.2. Effect of Additives on the Release of Inorganic Elements. *3.2.1. Effect of Additives during Laboratory-Experiments.* To reduce the release of P species during combustion, a widely used method is to inject Ca-based additives,^{2,4} which will react with the gaseous P and form Ca-phosphates with a high melting temperature. In this work, the presence of such reactions has been examined by mixing KH_2PO_4 and $\text{Ca}(\text{OH})_2$ at a molar ratio of 1:1, and then heating the mixture to 1500°C at a rate of $10^\circ\text{C}/\text{min}$ in a high temperature oven. If no reaction takes place between KH_2PO_4 and $\text{Ca}(\text{OH})_2$, the expected mass loss of the mixture is about 73.3 wt % at 1500°C , meaning that KH_2PO_4 is fully vaporized and CaO is the only residual product. However, the mass loss obtained in

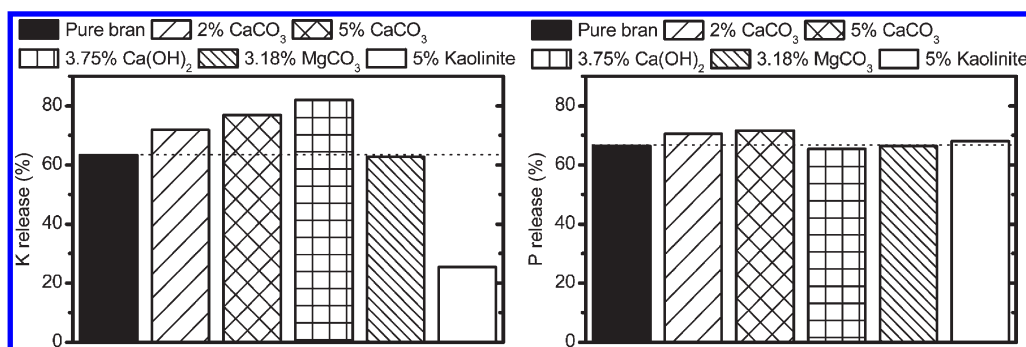


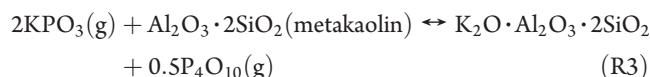
Figure 7. Influence of different additives on the release of K and P from bran combustion at 1100 °C. The percentage of additives is on weight basis.

the experiment was 16.2 wt %. This leads to the hypothesis that KCaPO_4 is formed during the heating of the mixture, and the vaporization of KCaPO_4 is negligible at 1500 °C. The hypothesis is supported by the fact that the theoretical mass loss of the KCaPO_4 formation reaction (17.1 wt %) is close to the measured mass loss (16.2 wt %). The result confirms that Ca-based additives can have a positive effect on the retention of phosphorus species during combustion. Two plausible global mechanisms, depending on whether reaction or thermal decomposition occurs first, are proposed below:



In the release experiments, selected additives (CaCO_3 , $\text{Ca}(\text{OH})_2$, MgCO_3 , or kaolinite) were mixed with bran, and the experiments listed in Table 2 were carried out. The combustion temperature for the additive experiments was chosen as 1100 °C, because the release of inorganic elements was found to be insignificant at other temperatures listed in Table 2. The effect of different additives on the release of K and P during bran combustion is shown in Figure 7. It can be seen that with the addition of Ca-based compounds (CaCO_3 and $\text{Ca}(\text{OH})_2$), the K release is increased by about 8–19%. A possible explanation for this is that the Ca-based compounds may react with the K-silicates or K-aluminosilicates in the bran and release part of the mineral-bounded K to the gas phase. The competition between the K and Ca for the reactive silicates or aluminosilicates has been observed previously.^{15,16} However, the presence of silicates or aluminosilicates may be limited in the bran ash, due to the small content of Al and Si. Therefore, the increased release of K during Ca addition may be related to the interactions between the K, Ca, and P species, because an increased Ca/P molar ratio in the mixture seems to be favored by the vaporization of K.¹⁵ The interpretations above may explain the observed increased release of K with increasing share of CaCO_3 (Figure 7). For different calcium compounds, it seems that when the same molar ratio of Ca/K is applied, $\text{Ca}(\text{OH})_2$ has a more significant effect on the release of K than the CaCO_3 . This may be linked to the particle size of the $\text{Ca}(\text{OH})_2$ and CaCO_3 used in the experiments, because the $\text{Ca}(\text{OH})_2$ particles are much smaller compared to CaCO_3 . Different from Ca-based additives, the addition of MgCO_3 shows a negligible effect on the release of K. However, the addition of kaolinite reduces the K release significantly, by about 75%. A primary reason for this is that the kaolinite reacts with gaseous K, resulting in formation of K-aluminosilicates. The reactions between kaolinite and gaseous alkali species are well-identified.^{16,37–41} In

the experiment with bran, it is suggested that a similar reaction may occur between kaolinite and the gaseous KPO_3 , with a plausible global mechanisms of



$\text{P}_4\text{O}_{10}(\text{g})$ is proposed as a product in the reaction above because it may be a thermodynamically favorable P species at high temperatures. However, the $\text{P}_4\text{O}_{10}(\text{g})$ may also react with other vaporized inorganic species, which will be discussed in detail in section 3.3. It should be noticed that the mechanism above is proposed on the basis of experimental observations. Further experiments and/or theoretical studies are needed to confirm the mechanism, which is beyond the scope of this work and is subjected to future work.

Compared to the case for K, the influence of additives on the release of P is generally not significant. With the addition of Ca-based compounds, almost no reduction in the P release is observed. These results seem to be in contrast with the performed test on the mixture of pure KH_2PO_4 and $\text{Ca}(\text{OH})_2$, showing that the release of P is negligible when the mixture is heated from room temperature to 1500 °C. The discrepancy may be explained by the high combustion temperature and the short contacting time between the gaseous P and Ca compounds in the experiments. According to the experimental procedures, char oxidation takes place at 1100 °C during the additive experiments. At this temperature, the KPO_3 formed from char combustion may be vaporized directly. However, when the mixture of KH_2PO_4 and $\text{Ca}(\text{OH})_2$ is heated from room temperature to 1500 at 10 °C/min, there will be a certain period that the KPO_3 is in molten phase. This molten phase together with a relatively long residence time may greatly promote the reaction between KPO_3 and Ca-additives. Besides, solid–solid reactions may happen between $\text{KH}_2\text{PO}_4/\text{KPO}_3$ and $\text{Ca}(\text{OH})_2$ during the heating. However, such reactions may be inhibited during the additive experiments, because the majority of P may be remaining as inositol phosphates before char oxidation. When the gaseous P is released from bran during char oxidation, the contact time between gaseous P and Ca-additives would be rather short in the reactor, as the fuel/ash bed is thin (a few millimeters) in the experiment. Therefore, the extent of reactions between gaseous P and Ca-additives is limited.

To evaluate the reactions between the bran ash and CaCO_3 at temperatures lower than 1100 °C, a mixture of bran ash produced at 700 °C and CaCO_3 was tested in the STA. As shown in Figure 8, when the mixture was heated from 25 to 1100 °C and maintained at 1100 °C for 6 h, the experimental mass loss was much lower

than that predicted from the pure components tested at the same conditions, by assuming an additive behavior of the mixed CaCO_3 and bran ash. This suggests that reactions between CaCO_3/CaO and bran ash have taken place and inhibited the vaporization of K and P species. A plausible mechanism for this reaction is given in (R2). The results support the hypothesis that the presence of molten phase P species over a relatively long residence time may be important for the reactions between the P species and Ca additives.

Compared to case with Ca additives, the reaction between gaseous K and kaolinite is found to be quite significant in the experiment with kaolinite addition. This implies that the reaction rate between the gaseous P and Ca-additives is likely much slower than that of kaolinite (or metakaolin at the experimental temperature) and gaseous K. Besides the Ca-additives, the addition of MgCO_3 or kaolinite also shows a negligible effect on the release of P.

The results from the additive experiments indicate that the Ca-based additives can promote the release of K, whereas the effect on P release may to a large extent depend on the experimental conditions. Still, this will lead to an increase of the molar ratio of the released K/P. As shown in Table 3, the molar ratio of K/P released during Ca-addition is in the range 0.96–1.18, which is larger than that of pure bran combustion (0.89). Besides the Ca-based additives, it can be seen that the addition of kaolinite significantly reduces the molar ratio of the released K/P to 0.37.

3.2.2. Effect of CaCO_3 Addition in Full-Scale Plant. To evaluate the effect of CaCO_3 addition on the release of K and P in the grate-fired plant, the molar ratios of K/P in the fly ash collected with and without CaCO_3 addition (5–8 wt %) are presented in Figure 9. It can be seen that the molar ratio of K/P in the fly ash from

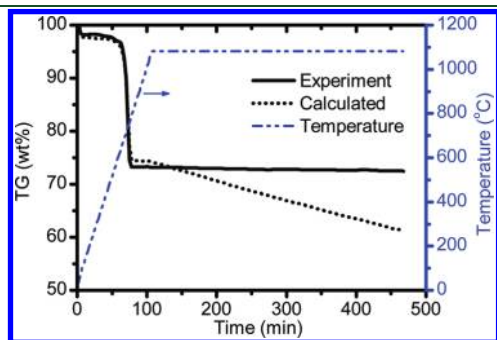


Figure 8. STA measurement of a mixture of bran ash from 700 °C and CaCO_3 (mass ratio 1:1.05, Ca/P molar ratio = 1.68), at 5% O_2 condition; the sample was heated from 25 to 1100 °C at a heating rate of 10 °C/min and then held at 1100 °C for 6 h.

CaCO_3 addition is normally above 1.5 and can even exceed 4. This is significantly higher than the ratio (0.9–1.2) found in the fly ash of pure bran combustion. The increased K/P molar ratio in the fly ash from CaCO_3 addition is presumably caused by an increased K release and/or a decreased P release. From Figure 9, it can be seen that the K/P molar ratio in the fly ash may vary significantly during the addition of CaCO_3 . This may be related to the variations in bran properties, CaCO_3 qualities, and the mixing between the CaCO_3 and bran.

Compared to laboratory-scale experiments, the effect of CaCO_3 addition seems to be more significant in the full-scale plant. This is probably due to that the bran combustion may start at a temperature lower than 1100 °C in the grate-fired plant. Therefore, the presence of molten K-phosphates may be possible over a relatively long residence time, which may promote the reaction between the Ca-additive and phosphates. In addition, the fuel/ash bed in the grate-fired plant is much thicker than that in the laboratory-scale experiment, which is a favorable condition for the reaction between gaseous phosphates and the Ca-additive.

3.3. Transformation of Vaporized Inorganic Elements in Bran Combustion. From previous sections, it was confirmed that the major inorganic elements released during bran combustion are K, P, S, and Cl (the Na is neglected here due to the relatively low content). In a grate-fired system, once these elements are released from the fuel bed, the interactions between these and other ash forming elements (such as Si and Ca) will be negligible, because the fly ash from a grate-fired system is dominated by flame-volatile inorganic species.³⁵ Although the vaporized inorganic elements during bran combustion are primarily K, P, S, and Cl, the interactions among these elements as well as with other organic elements such as C, O, and H are still rather complicated.^{13,14,34,42,43} According to the experiments carried out in a SCR reactor,³⁴ polyphosphoric acid could be formed in a short residence time (~a few seconds) when H_3PO_4 aqueous solution was sprayed to high temperature reactor (>850 °C) and subsequently cooled to a temperature below 500 °C. When the H_3PO_4 solution was replaced by a K_3PO_4 solution, more complicated transformations of the P and K species occurred and conceivably led to the formation of K and P compounds such as KH_2PO_4 , K_2HPO_4 , KOH, and H_3PO_4 .⁴² For a mixture of KCl, $\text{Ca}(\text{OH})_2$, H_3PO_4 , and H_2SO_4 ,⁴³ the composition of the fine particles formed during flue gas cooling showed that no Cl was present in the particles, suggesting that the Cl was mainly present in gas phase as HCl. All of the other inorganic elements were found in fine particles, and the formation of polyphosphoric acid was considered to be possible.⁴³ A recent experiment conducted in a circulating fluidized bed (CFB) boiler showed that the injection of $(\text{NH}_4)_2\text{HPO}_4$ before the convective part of the boiler

Table 3. Molar Ratio of the Released Inorganic Species in Different Experiments Combusted at 1100 °C

experiment no.	sample	molar ratio of the released inorganic species		
		K/P	K/Cl ^a	K/2S
9	bran	0.89	10.54	1.78
10	bran + 2 wt % CaCO_3	0.96	11.96	2.03
11	bran + 5 wt % CaCO_3	1.01	12.84	2.18
12	bran + 3.75 wt % $\text{Ca}(\text{OH})_2$	1.18	13.66	2.35
13	bran + 5 wt % kaolinite	0.37	4.48	0.76
14	bran + 3.18 wt % MgCO_3	0.89	10.46	1.76

^aThe Cl release is assumed to be 100%, as the Cl content in the residue ash is below the detection limit.

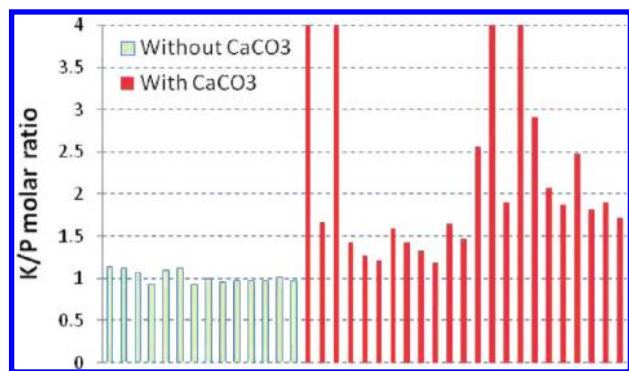


Figure 9. K/P molar ratio in the fly ash collected from the grate-fired plant without CaCO₃ and with CaCO₃ addition. The maximum value shown in the figure is 4.

could significantly reduce the KCl concentration in flue gas.⁴⁴ This clearly identified that K-phosphates would be more stable (or thermodynamically favorable) than the KCl at high temperature, which was in-line with the fine particle results obtained in.⁴³ The main P products formed during the injection of (NH₄)₂HPO₄ was considered to be KPO₃ and K₃PO₄.⁴⁴

To study the transformation of inorganic elements during bran combustion, equilibrium calculations have been performed in a temperature range from 25–1100 °C. The calculations were carried out on a simplified combustion system containing C, N, O, H, S, Cl, P, and K. The elements Si, Ca, Mg, Al, Fe, Ti, and Mn were neglected in the calculation, as these elements generally have low volatility in a grate-fired system. Na was also excluded in the thermodynamic calculation due to the small Na content in the bran as shown in Table 1.

The calculations were performed by using the commercial software HSC, version 6.1. The detailed database used in the calculation is listed as Supporting Information. The compounds with thermodynamic data not fully available for the studied temperature range (25–1100 °C) are specified. It is shown that for a large number of P compounds such as H₃PO₄, KH₂PO₄, K₂HPO₄, KPO₃, K₃PO₄, K₄P₂O₇, and P₄O₁₀(g), thermodynamic data are only available for temperatures up to 800 °C. It indicates that in the temperature range ~800–1100 °C, the thermodynamic data of these compounds are extrapolated from that of lower temperatures. This will to some extent influence the results obtained in the high temperature range, suggesting that the results below 800 °C are relatively more reliable. In addition, it should be noted that the thermodynamic data of some P compounds, such as polyphosphoric acids, are not available in the HSC database. This will also limit the reliability of the equilibrium calculations.

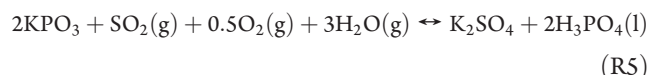
Besides the uncertainties of the database, equilibrium modeling itself also has a lot of limitations, which has been discussed throughout.^{45,46} This approach generally ignores the physical constraints such as mixing and reaction time, and chemical kinetic limitations of a combustion system. Thus the results predicted by equilibrium modeling may not represent a real combustion system. However, it will still provide valuable information regarding the possible reaction pathways and the qualitative influence of different parameters on a combustion system.^{45,46} This suggests that the results obtained from equilibrium modeling should be preferably treated qualitatively, rather than quantitatively. The limitations of the thermodynamic database and the modeling approach need to be considered in interpreting and applying the results.

The input data of the equilibrium calculations were based on the bran composition shown in Table 1. Because the K/P molar ratio in the fly ash from the grate-fired plant can vary significantly during operation (Figure 9), the calculations were performed at different K/P molar ratio conditions. To simulate the conditions in the plant, the moisture content of the bran was assumed to be 10 wt % and the excess air ratio used in the simulation was 1.2. The S and Cl in the bran were assumed to be totally released to the flue gas. For P and K, three different conditions were applied in the simulations: in condition A, it was assumed 70% of the K and P in the bran were released to the flue gas; in condition B, the release of K was 30% and the release of P was 70%; in condition C, the release of K was 70% and the release of P was 30%. The main objective to perform calculations at these three conditions was to evaluate the influence of K and P release on ash transformations in flue gas.

Figure 10a shows the equilibrium compositions of the K and P species obtained at condition A, in which it is assumed that 70% of the K and P in the bran are released to flue gas. The results are representative for pure bran combustion condition. It can be seen that the KPO₃ is the only stable K species at temperatures higher than 400 °C. When the temperature is decreased from 400 °C, KH₂PO₄ and K₂SO₄ gradually become the major stable K species. Similar tendencies are also seen in the distribution of P species. At temperatures higher than 500 °C, the major P species is KPO₃, followed by about 6% P₄O₁₀(g). The presence of P₄O₁₀(g) is related to the K/P molar ratio used in this simulation, which is below 1. When the temperature is decreased from 500 to 450 °C, the majority of the P₄O₁₀(g) is converted to H₃PO₄(l). The plausible global mechanism for this conversion is



At temperatures lower than 400 °C, the KPO₃ starts to convert to H₃PO₄ and/or KH₂PO₄, with plausible global mechanisms of



Thermodynamic calculations in Figure 10a predicted the presence of liquid phase H₃PO₄(l) at temperatures below 500 °C. Experimentally, it was found that the presence of polyphosphoric acid at temperatures lower than 500 °C was possible, in a form of submicrometer liquid particles.³⁴ However, in the thermodynamic calculations of this work, the formation of polyphosphoric acids was neglected, due to the absence of thermodynamic data for these compounds.

When the bran is mixed with kaolinite or silicates, the release of K to the gas phase may be inhibited. To simulate such a situation, thermodynamic calculations were performed by assuming the release of K is 30% and the release of P remains 70% (condition B). The equilibrium composition of K and P species obtained under this condition is shown in Figure 10b. It can be seen that the dominant K species above 400 °C is still KPO₃. In the temperature range 400–200 °C, the KPO₃ is progressively converted to K₂SO₄ and KH₂PO₄. At temperatures below 200 °C, K₂SO₄ becomes the major stable compound. The distribution of P species in condition B is quite different from that in condition A. In Figure 10b, it is seen that the major P species above 500 °C is P₄O₁₀(g), followed by about 40% KPO₃.

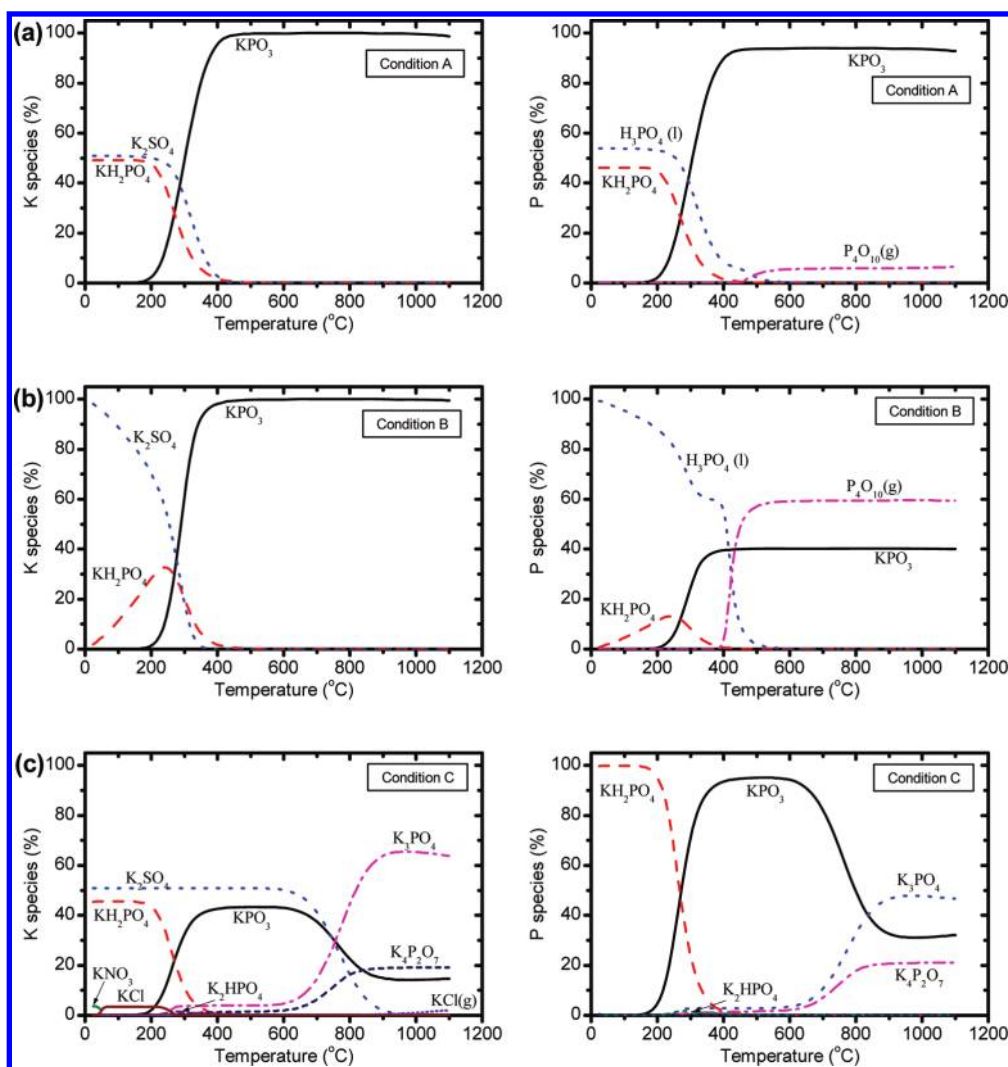
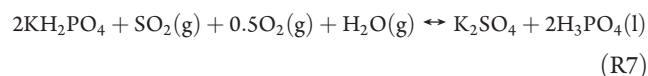


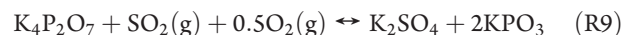
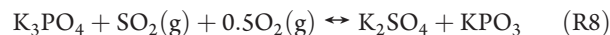
Figure 10. Equilibrium compositions of the K and P species at (a) condition A (assume 70% K and 70% P release, with K/P molar ratio = 0.94 and K/2S molar ratio = 1.96), (b) condition B (assume 30% K and 70% P release, with K/P molar ratio = 0.40 and K/2S molar ratio = 0.84), and (c) condition C (assume 70% K and 30% P release, with K/P molar ratio = 2.19 and K/2S molar ratio = 1.96).

Due to the large fraction of $P_4O_{10}(g)$, the formation of H_3PO_4 from $P_4O_{10}(g)$ is significant in the temperature range 400–500 °C. Below 400 °C, the KPO_3 starts to convert to H_3PO_4 and KH_2PO_4 . The KH_2PO_4 may be further converted to H_3PO_4 , at temperature lower than 250 °C, with a plausible global mechanism of



As mentioned above, Ca-based additives can inhibit the release of P and promote the release of K during bran combustion. Therefore, the molar ratio of the released K/P can be increased by adding Ca. To simulate such a situation, thermodynamic calculations have been conducted according to condition C, which assumed that the release of K is 70% and the release of P is 30% in bran combustion. The simulation results are shown in Figure 10c. It can be seen that the distribution of K species is rather complicated at this condition. At a temperature higher than 800 °C, the main stable K species are K_3PO_4 , $K_4P_2O_7$, and KPO_3 , followed by a small amount of $KCl(g)$. In the temperature range

400–800 °C, the dominant K species become K_2SO_4 and KPO_3 , which is presumably a result of the following plausible global mechanisms:



One should be aware that the mechanisms above (also other mechanisms involving sulphation reactions) may be significantly limited by the oxidation of SO_2 to SO_3 . Thus the actual conversion may be orders of magnitude lower than that predicted from equilibrium calculations. More fundamental experiments are needed to validate these mechanisms in practical conditions, which is outside the scope of this work.

When the temperature is decreased from 400 to 200 °C, a transition from KPO_3 to KH_2PO_4 is observed. At temperatures lower than 200 °C, the presence of a small amount of KCl and KNO_3 is predicted. For P species, it is seen that the major P species above 800 °C are K_3PO_4 , KPO_3 , and $K_4P_2O_7$. With decreasing temperature, transitions from K_3PO_4 and $K_4P_2O_7$ to KPO_3 happen between 800 and 600 °C. When the temperature becomes

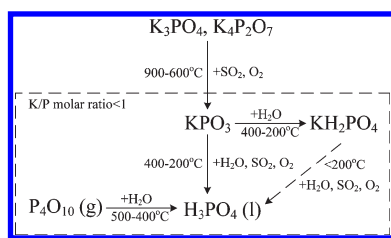


Figure 11. Proposed reaction pathways of the phosphorus containing species, based on equilibrium calculations.

lower than 400 °C, a transformation from KPO_3 to KH_2PO_4 occurs. Below 200 °C, the P species is dominant by KH_2PO_4 . Compared with the distribution of P species in Figure 10a,b, it is found that the presence of $\text{H}_3\text{PO}_4(\text{l})$ is negligible in Figure 10c, indicating that the formation of H_3PO_4 may be prevented by a large K/P molar ratio in flue gas.

According to the thermodynamic calculations, the possible reaction pathways of the P containing species in the flue gas are proposed, as shown in Figure 11. It is seen that when the molar ratio of the released K/P is below 1, KPO_3 and $\text{P}_4\text{O}_{10}(\text{g})$ are the dominant stable K and P species at temperatures above 500 °C. During flue gas cooling, the $\text{P}_4\text{O}_{10}(\text{g})$ can be converted to $\text{H}_3\text{PO}_4(\text{l})$ in the temperature range 500–400 °C, whereas the KPO_3 can be transformed to either KH_2PO_4 or $\text{H}_3\text{PO}_4(\text{l})$, in the temperature range 400–200 °C. Although such pathways seem to be thermodynamically feasible, the conversion of KPO_3 to $\text{H}_3\text{PO}_4(\text{l})$ may be kinetically limited, due to the relatively low temperature and low concentration of SO_2 in flue gas. The conversion of $\text{P}_4\text{O}_{10}(\text{g})$ to H_3PO_4 may more likely happen, as the concentration of H_2O will be much higher than that of SO_2 . The experimental results in the literature also support that this may be a feasible pathway for the formation of $\text{H}_3\text{PO}_4(\text{l})$, or polyphosphoric acids, which are not considered in the thermodynamic calculations.³⁴ Below 200 °C, thermodynamic calculation predicts a conversion of KH_2PO_4 to $\text{H}_3\text{PO}_4(\text{l})$, when the K/2S molar ratio is 0.84 (Figure 10b). However, such conversion is not predicted when the K/2S molar ratio is 1.96 (Figure 10c).

When the molar ratio of the released K/P is high (e.g., >2), the stable P species at temperatures above 600 °C will be KPO_3 , K_3PO_4 , and $\text{K}_4\text{P}_2\text{O}_7$. According to thermodynamic calculations, K_3PO_4 and $\text{K}_4\text{P}_2\text{O}_7$ may be converted to KPO_3 and K_2SO_4 in the temperature range 900–600 °C, through reacting with SO_2 and H_2O . The formed KPO_3 will be primarily converted to KH_2PO_4 in the temperature range 400–200 °C. The formation of $\text{H}_3\text{PO}_4(\text{l})$ is not likely to happen under this condition, unless extra SO_2 is available for reacting with KPO_3 .

One should be aware the reaction pathways proposed in Figure 11 are based on the equilibrium calculation results. Therefore, it has been naturally influenced by the limitations of equilibrium modeling, which have been discussed previously. To minimize these limitations, more reliable thermodynamic data regarding P species need to be developed, which is outside the scope of the present work. In addition, it is also favored to develop detailed kinetic models for the P related species.

3.4. Practical Implications. The results from the present work have some practical implications for a grate-fired plant utilizing bran or similar P-rich fuel. To reduce K and P release during bran combustion, addition of Ca-based additives such as CaCO_3 and $\text{Ca}(\text{OH})_2$ is a feasible solution, as it may reduce

both the K and P release through a plausible mechanism proposed in (R2). On the other hand, the Ca-based additives may also react with K-phosphates or K-silicates/K-aluminosilicates in bran and thereby release the K to the gas phase. A combination of the mechanisms mentioned above will increase the molar ratio of K/P released to gas phase, which is confirmed by the full-scale data shown in Figure 9. The effect of Ca addition seems to be sensitive to the injection method. The effect would be more pronounced when the Ca additive is premixed with bran before combustion. This is likely related to the presence of molten phase phosphate over a relatively long residence time, which may promote the reaction between Ca additive and phosphate. The reaction rate between gaseous P and Ca additives is probably quite low, at least much lower than that of kaolinite and gaseous alkali species. Therefore, injection of Ca additive directly to the flue gas may not significantly reduce the vaporized K and P species. Besides Ca based additives, addition of kaolinite can greatly reduce the release of K via a plausible mechanism proposed in (R3), whereas the effect on P release is insignificant. It therefore will cause a significant decrease of the molar ratio of K/P released to gas phase.

The formation of fine particles during bran combustion may primarily be related to the quantity of K and P released on the grate. However, for other ash related problems, such as deposits formation and corrosion, the fly ash chemistry in flue gas also plays a significant role. Thermodynamic calculations indicate that the distribution of P species in flue gas is quite sensitive to the molar ratio of the released K/P. As seen in Figure 10a,b, KPO_3 and $\text{P}_4\text{O}_{10}(\text{g})$ are the main inorganic species present in flue gas at temperatures above 500 °C, when the molar ratio of the released K/P is below 1. Because the melting temperature of KPO_3 is approximately 800 °C (Figure 4) and the $\text{P}_4\text{O}_{10}(\text{g})$ is present in the gas phase at temperatures above 500 °C, it is likely that the deposit built up in the superheaters may not be significant if the flue gas temperature in the convective part of the boiler is below 800 °C, as the formed deposits may be in powdery and nonsticky form, which can be easily removed by soot-blowing. This hypothesis is supported by the observations in the grate-fired plant. However, when the flue gas temperature becomes lower than 500 °C, part of the KPO_3 and $\text{P}_4\text{O}_{10}(\text{g})$ may be converted to $\text{H}_3\text{PO}_4(\text{l})$. The presence of liquid phase $\text{H}_3\text{PO}_4(\text{l})$ may increase the deposit built-up in the economizers of the grate-fired boiler, which is normally operated at a flue gas temperature of 200–400 °C. To minimize the deposit buildup in the economizers, a possible solution is to increase the molar ratio of K/P and K/S in the flue gas. As shown in Figure 10c, the presence of $\text{H}_3\text{PO}_4(\text{l})$ becomes negligible, when the molar ratio of K/P and K/2S is about 2.19 and 1.96, respectively. In addition, at this condition, >the stable main P species at temperatures above 800 °C become K_3PO_4 , $\text{K}_4\text{P}_2\text{O}_7$, and KPO_3 . Both K_3PO_4 and $\text{K}_4\text{P}_2\text{O}_7$ have higher melting temperatures than KPO_3 ,³³ which may be more favorable with respect to the deposit buildup. Therefore, to minimize the deposit buildup in the convective part and economizer of the boiler, a higher molar ratio of K/P in the flue gas may be desirable. One should be aware that if both the molar ratio of K/P and the Cl content in the flue gas is significantly high, it will lead to the formation of KCl, which will cause severe corrosion problems. However, in P-rich fuels, the Cl content is normally quite low, thus the formation of KCl will probably not be important during combustion of these fuels.

4. CONCLUSION

In the present work, the release and transformation of inorganic elements during combustion of a residual bran from bioethanol production were characterized. Through a literature review and SEM-EDS analysis of the bran, it was suggested that a large fraction of the P, K, and Mg in the seed-originated biofuels may be present as phytic acid/phytate or other inositol phosphates. By performing experiments in a horizontal tube reactor, the main inorganic elements released during bran combustion were found to be K, P, and S, supplemented by Cl and Na. The S in bran was almost totally vaporized during bran pyrolysis at temperatures below 700 °C. About 60–70% of the K and P in bran were released in the temperature range 900–1100 °C during bran combustion. The release of K and P was presumably related to the vaporization of the KPO_3 generated from thermal decomposition of inositol phosphate. The release results obtained in the laboratory experiments were in agreement with the observations from a grate-fired plant using similar fuel. On the other hand, the release mechanism we proposed requires confirmation through further investigations such as XRD analysis on the residue ash obtained at different temperatures as well as through sampling and characterization of the released K and P species.

The effect of additives such as $CaCO_3$, $Ca(OH)_2$, and kaolinite on the release of inorganic elements during bran combustion was studied in a horizontal tube reactor. The addition of Ca-based additives promoted the vaporization of K, whereas the influence on P release was insignificant. For the addition of kaolinite, the release of K was significantly inhibited, while the release of P was almost unaffected. Comparing the laboratory results with that of full-scale plant revealed that the effect of Ca-based additive was more pronounced in the full-scale plant, as the addition of Ca-based additive greatly increased the molar ratio of K/P in flue gas. The discrepancies between the experimental and full-scale implied that the presence of molten phase phosphate over a relatively long residence time may be important for the reaction between Ca-based additive and phosphate.

Thermodynamic calculations based on a simplified system indicated that the molar ratio of the released K/P could greatly influence the fly ash chemistry. With a molar ratio of K/P lower than 1, KPO_3 and $P_4O_{10}(g)$ were the major stable K and P species at temperatures higher than 500 °C. Below 500 °C, part of the KPO_3 and $P_4O_{10}(g)$ were converted to $H_3PO_4(l)$, which might cause severe deposit buildup in the economizers of the grate-fired boiler. However, by increasing the molar ratio of the released K/P, the ash chemistry could be changed significantly and the formation of $H_3PO_4(l)$ might not be thermodynamically favorable. On the basis of thermodynamic calculations, the transformation mechanisms of the K and P species in the flue gas have been proposed. However, it should be noted that the results/mechanisms derived from the thermodynamic calculations are restricted by the reliability of the thermodynamic data as well as a number of factors that have not been considered in calculations, such as reaction rate, residence time, and mixing. Thus the mechanisms proposed require further validations through fundamental experiments or theoretical studies, which is beyond the scope of this work.

Practical implications of the present work were discussed. It was suggested that Ca-based additives could be used to reduce the release of P and to some extent increase the release of K during grate-firing of bran, whereas kaolinite could be applied to inhibit

the release of K. The effect of Ca addition might be more pronounced if it was premixed with fuel before combustion. The molar ratio of K/P in flue gas could be increased by Ca-based additives, which is a favorable condition for minimizing deposit buildup in the convective part and economizer of the boiler.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed database used in the thermodynamic calculations by the software HSC 6.1. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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