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Influence of the Atmosphere on the Transformation of Alkali and Alkaline Earth Metallic Species during Rice Straw Thermal Conversion

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ABSTRACT: The influence of the atmosphere on the transformation of alkali and alkaline earth metallic (AAEM) species during rice straw thermal conversion was investigated by a fixed-bed reactor at 1073, 1173, and 1273 K. Two types of atmospheres were considered: 100% (v/v) N₂ to simulate pyrolysis and 1% (v/v) O₂ in N₂ balance to simulate combustion. The release of the AAEM species during pyrolysis and combustion of the rice straw was quantified by a mass balance based on the weight measurements and inductively coupled plasma (ICP) analysis of the rice straw and the solid residue. Solid residues and released and condensed particles obtained in experiments were processed by water leaching and 1% HNO₃ washing and analyzed by ion chromatography (IC) to determine the possible chemical form of the AAEM species contained in them. The experimental results showed that the oxidizing atmosphere facilitated the release of K at 1073, 1173, and 1273 K by enhancing the decomposition of K₂CO₃ and char K in the char during the char combustion stage of the rice straw combustion experiment. However, the oxidizing atmosphere suppressed the release of Na, Ca, and Mg at 1073, 1173, and 1273 K. For Na, the release suppression was caused by its promoted interaction with silicate in the oxidizing atmosphere. For Ca and Mg, such suppression was supposed to be caused by the suppressing effect of the oxidizing atmosphere on the release of Ca and Mg from char Ca and char Mg in the char of the rice straw.

1. INTRODUCTION

To alleviate global environmental problems, biomass, as a renewable and CO₂-neutral energy resource, is a promising fuel for future energy production. However, technical challenges arose in using biomass as a fuel. The most severe problem came from the formation of high mass loadings of aerosols and deposition of potentially corrosive components on heat-transfer surfaces in the biomass combustion, gasification, and pyrolysis reactors.^{1–4} Investigations of the aerosols and fly ashes in the wood combustion systems showed that volatile alkali metals K and Na, as well as S and Cl, are the most important aerosol-forming elements.⁵ High amounts of K, Cl, and S were also found to release to the gas phase and form the fly ash during the combustion of annual biomass on a grate.^{6,7} In the bottom ash and the slags of a cereal burner, K, Ca, Mg, P, and Si were found to be the main components.⁸ Besides, the biomass generally contains a relatively high amount of alkali and alkaline earth metallic (AAEM) species. Therefore, a better understanding of the transformation of the AAEM species in the biomass during thermal treatment will help to solve the technical problems brought using the biomass as a fuel.

It is proven that the temperature of the thermal treatment significantly influences the release amount of the AAEM species from the biomass. Jensen et al.⁴ demonstrated that, below 973 K, no significant K release was observed during the pyrolysis of the wheat straw in the fix-bed reactor and, above 973 K, K release increased progressively until about 25% at 1323 K. Knudsen et al.⁶ also reported that K was released to the gas phase in significant amounts above 973 K during the combustion of six different kinds of annual biomass in grate combustion conditions and between 50 and 90% of the total K was released to the gas

phase at 1323 K. During the combustion of four different kinds of wood in a laboratory-tube reactor, van Lith et al.⁹ found that the release of K started around 773–873 K and increased sharply in the temperature range of 1073–1273 K, whereas the release of Na gradually increased from 773 to 1273 K, followed by a sharp increase to 1423 K. The release of the AAEM species was also investigated using a wire-mesh reactor during the pyrolysis of pine sawdust by Okuno et al.¹⁰ They found that the release of AAEM species increased in the temperature range from 773 to 1073 K: the release of K started around 673 K and reached 60% at 1073 K; the release of Na was similar to that of K; and the release of Ca and Mg started around 873 K and reached ~20% at 1073 K. Therefore, it can be concluded that a generally significant release of the AAEM species from the biomass occurred when the thermal treatment temperature was above 1073 K.

The content of Si and Cl in the biomass was also proven to be an important factor that could influence the release of K and Na in the biomass. Knudsen et al.^{6,7} found that the biomass fuels with an appreciable content of silicate showed the lower release of K, but a significant fraction of the fuel K could also be released from high silicate biomass fuels if they also contain high amounts of Cl. van Lith et al.⁹ also found that less K was released from the biomass with a lower K/Si ratio during the wood combustion from 1073 to 1273 K. Such an influence of Si and Cl was also reported in the area of coal combustion. Neville and Sarofim¹¹ combusted four different kinds of coals and found that Na appearing in the fume increased with an

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increasing Cl/Na ratio and decreased with an increasing silica content in the parent coal.

Particle size,¹² carrier gas velocity,¹³ and heating rate¹⁴ were also reported to be able to influence the release of the AAEM species from the biomass. However, more experimental evidence is still needed to prove that the underlying mechanisms of these influence factors applied for a broader range of biomass types and thermal treatment conditions.

The atmosphere also plays an important role in the release of the AAEM species during the biomass thermal treatment process. Knudsen et al.⁶ found that an insignificant amount of K is released during wheat straw pyrolysis (25 min), while 20–50% K is released during wheat straw combustion at 1173 K. This difference was attributed to the atmosphere; however, detailed analysis information about the products were too deficient to investigate the mechanism of how the atmosphere influenced K release. For coal combustion, Li et al.^{15,16} pointed out that the atmosphere surrounding the coal particle seemed to be critical for the release of the AAEM species (Na, Ca, and Mg) and believed that an oxidizing atmosphere greatly helped to retain the AAEM species in the solid phase. From the above research, we can see that the atmosphere influences the release of K from biomass and the release of Na, Ca, and Mg from coal and the influences under the two cases were different because of fuel properties. However, how the atmosphere influences the release of Na, Ca, and Mg from biomass and how the atmosphere influences the release of AAEM species from the biomass in a wide temperature range are not yet clear.

In this work, pyrolysis and combustion experiments with rice straw were developed to compare the transformation of AAEM species under different atmospheres. The mechanisms of how the atmosphere influences the release of the AAEM species were also discussed.

2. EXPERIMENTAL SECTION

2.1. Fuel. Rice straw was first pulverized in a cutting mill with a 150 μm screen, and the fines with a diameter between 98 and 125 μm were subsequently selected by an electric vibrating screen. The selected rice straw particles were then dried at 378 K for 10 h and sealed prior to use. The elemental composition and the content of the ash-forming elements of the rice straw in the resulting size fraction were presented in Table 1.

2.2. Experimental Apparatus and Procedures. A fixed-bed reactor shown in Figure 1 was developed to investigate the influence of the atmosphere on the AAEM species transformation during the thermal conversion of the rice straw. The fixed-bed reactor consisted of a quartz reactor shell and a removable quartz basket (inner diameter of 18.0 mm and height of 60 mm) with a quartz filter (Staplex, New York, NY; pore size of 0.1 μm) and a quartz frit inside. The basket was connected with quartz tube 1 by a ground quartz glass joint, as well as quartz tube 1 with quartz tube 2. At the connecting position of quartz tube 1 and quartz tube 2, quartz filter 2 was inserted to filter fully and sample the condensed particles in the flue gas in the purpose of further analysis. At the back of quartz tube 2, a quartz glass wool filter was inserted to capture the newly formed particles in the flue gas after passing quartz filter 2. After the quartz glass wool filter, the flue gas was cooled and subsequently led to O₂, CO, and CO₂ analyzers.

Two types of atmospheres were considered here: 100% (v/v) N₂ to simulate pyrolysis and 1% (v/v) O₂ in N₂ balance to simulate combustion. The experimental temperatures were 1073, 1173, and 1273 K. The purpose of choosing the concentration of O₂ in N₂ balance to be 1% (v/v) to simulate combustion was to avoid temperature overshoot and to minimize its difference with the temperature history of the rice straw pyrolysis experiment (<6 K measured at the set-point temperature of 1173 K).

Table 1. Composition of the Rice Straw

Proximate Analysis (wt %, Dry Basis)	
ash	13.93
volatile matter	68.53
fixed carbon	17.54
Ultimate Analysis (wt %, Dry and Ash-Free Basis)	
C	47.92
H	6.27
O (by difference)	44.38
N	1.17
S	0.26
Main Ash-Forming Elements (wt %, Dry Basis)	
Si	4.14
Al	0.0065
Fe	0.03
Ca	0.64
Mg	0.21
K	2.26
Na	0.09
Cl	0.34
P	0.10

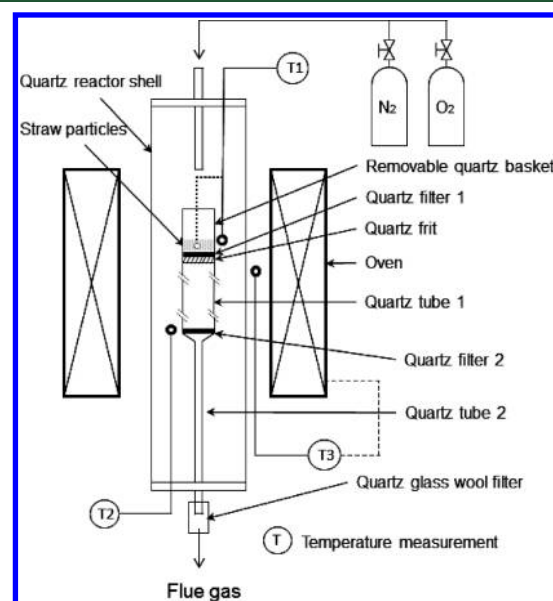


Figure 1. Sketch of the fixed-bed reactor.

The experiments were carried out as follows: a sample of approximately 1.5 g of rice straw particles was placed above the quartz filter 1, which was supported by the quartz frit inside the quartz basket. When the desired temperature inside the reactor was reached and stabilized, the reactor was purged with N₂ or 1% (v/v) O₂ in N₂ balance, depending upon the desired atmosphere. The basket was then inserted into the reactor. The distance between the quartz filter 2 and the end of the quartz reactor shell was adjusted and set in advance to keep the holding area of quartz filter 2 in the temperature range of 873 \pm 10 K. The flow rate of the gas was controlled by the mass flow controller to maintain a constant residence time of 0.6 s inside the quartz basket. The temperature at the outside surface of the quartz basket and the flue gas composition were acquired and monitored on line during the experiments. When no more CO or CO₂ (<10 ppm) could be detected in the flue gas, the heating of the oven was stopped and a gas flow of pure nitrogen was added between the quartz reactor shell and the oven to cool the reactor. When the temperature of the quartz basket decreased to 423 K, the sample was withdrawn from the reactor and cooled to room temperature under ambient conditions. Times of 60 and 180 min were set for the rice straw pyrolysis and

combustion experiments, respectively, at all three temperatures considered in this study.

The release of the AAEM species during pyrolysis and combustion of the rice straw was quantified by a mass balance based on the weight measurements and chemical analysis of the rice straw and the solid residue obtained in the quartz basket at the three chosen temperatures. The solid residue were dissolved by pressurized acidic digestion in HF/HNO₃/H₂O₂, and the element concentrations of the AAEM species were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (Thermo Elemental, Franklin, MA). For convenience, the solid residue was designated as char and ash for the rice straw pyrolysis and combustion experiments, respectively, hereafter.

After pyrolysis and combustion of the rice straw in this fixed-bed reactor, deposits were formed inside quartz tube 1 and quartz tube 2. Condensed particles in the flue gas were also collected on quartz filter 2. The AAEM species contained in these deposits and particles were recovered in the rice straw pyrolysis and combustion experiments conducted at 1173 K. Briefly, after each rice straw pyrolysis or combustion experiment conducted at 1173 K, quartz tube 1, quartz tube 2, and quartz filter 2 were withdrawn from the reactor and immersed into the 1% HNO₃ solution in separate bottles. After being washed in the ultrasonic bath for 1 h at 333 K, the AAEM species in the extracts were subsequently quantified by ICP–AES.

Information about the fraction and the chemical form of the water-soluble AAEM species in the rice straw, the char and ash samples, and the particles collected on quartz filter 2 obtained in rice straw pyrolysis and combustion experiments at 1173 K were acquired by a water leaching experiment.⁴ Briefly, 0.5 g of rice straw, 0.2 g of ground char and ash samples, and the whole piece of the quartz filter 2 with condensed particles on it were added in 50 mL of deionized water in separate bottles and were washed in the ultrasonic bath for 2 h at 333 K. The AAEM species contents in each extract were determined by ICP–AES. The concentrations of the anions in the extracts were analyzed by ion chromatography (IC) (Dionex, Sunnyvale, CA).

Here, we believed^{4,6} that the silicates of AAEM species were the only AAEM-species-containing components presented in the rice straw, char, and ash that were not dissolved by HNO₃. Therefore, to investigate the possible binding of the AAEM species to silicates, 0.5 g of rice straw and 0.2 g of ground char and ash samples obtained in rice straw pyrolysis and combustion experiments at 1173 K were dissolved in 1% HNO₃ solution and were washed in the ultrasonic bath for 2 h at 333 K. The AAEM species contents in the extract were subsequently quantified by ICP–AES.

The morphology and association of the elements in the particles collected on quartz filter 2 obtained in rice straw pyrolysis and combustion experiments at 1173 K and the ash obtained in rice straw combustion experiments at 1173 K were studied using scanning electron microscopy in combination with energy-dispersive X-ray (SEM–EDX) (Hitachi S5500, Japan).

An additional experiment was conducted in which 1.5 g of rice straw first underwent pyrolysis in a N₂ atmosphere at 1173 K for 60 min, and then the inlet gas was shifted to 1% (v/v) O₂ in N₂ balance and lasted for an extra 180 min. This experiment was performed repeatedly and was termed the char combustion experiment hereafter. The release of the AAEM species during the char combustion experiment was also quantified by a mass balance based on the weight measurements and chemical analysis of the rice straw and the solid residue obtained in the quartz basket.

3. RESULTS

3.1. Distribution and Release of the AAEM Species. In Figure 2, the distribution of the AAEM species content in the solid residue, the deposits on quartz tubes 1 and 2, and the collected particles on quartz filter 2 during rice straw pyrolysis and combustion experiments at 1173 K are presented. The spread of the total recovery of the AAEM species in repeated experiments was less than 5%, indicating that the uncertainty of the recovery experiments was acceptable. It can also be seen

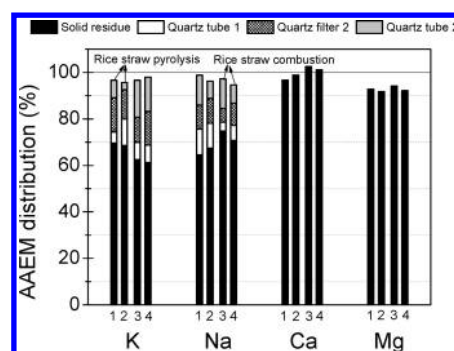


Figure 2. Distribution of the AAEM species during repeated rice straw pyrolysis experiments (numbered 1 and 2) and rice straw combustion experiments (numbered 3 and 4) at 1173 K.

that K and Na were distributed among all samples, and more than 95% of them in the rice straw were recovered by 1% HNO₃ washing after both rice straw pyrolysis and combustion experiments at 1173 K. The concentrations of Ca and Mg in the 1% HNO₃ extracts of the deposits on quartz tubes 1 and 2 and the collected particles on quartz filter 2 were all lower than the limit of the quantification of ICP–AES (0.5 ppm for Ca and 0.1 ppm for Mg); therefore, the fraction of them in these samples was considered to be 0. It is also seen that the Ca fraction in the solid residue during rice straw combustion experiments at 1173 K slightly exceeded 100%. This was considered to be due to the inhomogeneity in the concentration of Ca in the rice straw. It is assumed that the fuel samples used in the rice straw combustion experiment had a higher Ca concentration than the analyzed rice straw samples, as presented in Table 1. Therefore, in reality, almost all Ca remained in the solid residue during the rice straw combustion experiment at 1173 K. The standard deviations of the concentration of the K, Na, Ca, and Mg contents in the rice straw were 1.2, 1.5, 2.5, and 1.5%, respectively, by analyzing seven repeated samples.

The release of the AAEM species during rice straw pyrolysis and combustion experiments at 1073, 1173, and 1273 K and char combustion experiments at 1173 K was presented in Figure 3. In the rice straw pyrolysis experiments, the release of the AAEM species all increased with the temperature. In the rice straw combustion experiments, the release of K and Na also increased with the temperature but the release of Ca and Mg changed little with the increase of the temperature. In addition, it was considered that, in reality, little Ca released to the gas phase in the rice straw combustion experiments.

It is clearly seen from Figure 3 that the release of K in the rice straw combustion experiments at all three temperatures was higher than that in the rice straw pyrolysis experiments. The release of Na, Ca, and Mg in the rice straw combustion experiments was lower than their release in the rice straw pyrolysis experiments at all three temperatures.

In the char combustion experiment at 1173 K, the release of K was even higher than that in the rice straw combustion experiment at 1173 K, whereas the release of Na was equal to its release in the rice straw pyrolysis experiment at 1173 K. For the release of Ca and Mg in the char combustion experiment, they were seen to be less than their release amount in the pyrolysis experiment at 1173 K.

The standard deviation of the release data of the AAEM species in this paper was determined by the standard deviations in the mass and elemental composition measurements of the rice straw and solid residue. Because of different homogeneities

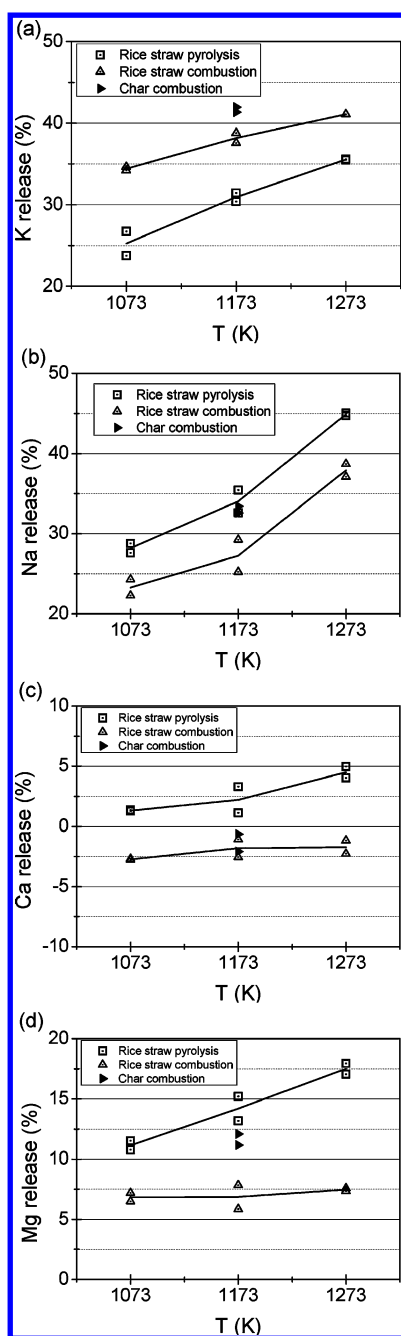


Figure 3. Release of (a) K, (b) Na, (c) Ca, and (d) Mg during rice straw pyrolysis and combustion experiments at 1073, 1173, and 1273 K and char combustion experiments at 1173 K.

of the different elements in the rice straw, the release of the AAEM species received different standard deviations. For the K, Na, Ca, and Mg release, the standard deviations of them were 2–3, 2–4, 3–6, and 2–4%, respectively. The standard deviations of the AAEM species release data decreased with the increase of the temperature. The spread of the AAEM species release data between repeated experiments was a maximum of 5%. This indicated that the uncertainty was on an acceptable level.

3.2. Chemical Form of the AAEM Species. The fractions and the chemical form information of the water-soluble AAEM species in the rice straw, char, and ash samples obtained in rice straw pyrolysis and combustion experiments at 1173 K acquired by the water leaching experiment were presented in

Tables 2 and 3. In Table 3, the charge balance was closed for the washing water of all samples, indicating that all important

Table 2. Fractions of the AAEM Species Water-Soluble in Rice Straw, Char (1173 K), and Ash (1173 K)

	K (%)	Na (%)	Ca (%)	Mg (%)
rice straw	100	99	7	52
char (1173 K)	80	93	6	3
ash (1173 K)	7	4	1	1

Table 3. Main Constituents in the Rice Straw, Char (1173 K), and Ash (1173 K) Washing Water

	Rice Straw				
	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	
cations (mmol/g)	0.589	0.055	0.034	0.009	
anions (mmol/g)	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	CO ₃ ²⁻	HCO ₃ ⁻
	0.177	0.051	0.026	N/A	0.219
	Char (1173 K)				
	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	
cations (mmol/g)	0.924	0.136	0.006	0.030	
anions (mmol/g)	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	CO ₃ ²⁻	HCO ₃ ⁻
	0.001	0.014	0.020	0.601	0.017
	Ash (1173 K)				
	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	
cations (mmol/g)	0.161	0.014	0.006	0.011	
anions (mmol/g)	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	CO ₃ ²⁻	HCO ₃ ⁻
	0.001	0.047	0.002	N/A	0.186

ionic components were detected. The fractions of the AAEM species that were not dissolved by 1% HNO₃ in the rice straw, char, and ash samples obtained in rice straw pyrolysis and combustion experiments at 1173 K were presented in Table 4.

Table 4. Fractions of the AAEM Species Insoluble in 1% HNO₃ in Rice Straw, Char (1173 K), and Ash (1173 K)

	K (%)	Na (%)	Ca (%)	Mg (%)
rice straw	0	0	0	0
char (1173 K)	9	0	30	35
ash (1173 K)	89	85	81	95

For rice straw, 100% K, 99% Na, 7% Ca, and 52% Mg in it were water-soluble, as shown in Table 2. The main anions in the washing water were Cl⁻ and HCO₃⁻, as presented in Table 3, indicating that the water-soluble fractions of the AAEM species were combined with them and existed in the form of inorganic salts in the rice straw. It is seen in Table 4 that the fractions of the AAEM species that are not soluble in 1% HNO₃ in the rice straw were all 0. This suggested that Ca and Mg in the rice straw that are not soluble in water possibly existed in the form of carbonate, phosphate, or sulfate or may be incorporated with organic structures of the rice straw, which could all be dissolved in 1% HNO₃.

For the char obtained in the rice straw pyrolysis experiments at 1173 K, it is seen in Table 2 that 80% K, 93% Na, 6% Ca, and 3% Mg in the char were water-soluble. The main anion in the washing water of the char was CO₃²⁻, as presented in Table 3. This indicated that the water-soluble fractions of K and Na in the char existed mainly in the chemical form of carbonate. In Table 4, it is seen that 9% K, 30% Ca, and 35% Mg in the char could not be dissolved in 1% HNO₃ and they were supposed to exist in the silicate form. Jensen et al.⁴ also

found that 20% K in the char obtained in the wheat straw pyrolysis at 1173 K could not be dissolved in the sulfuric acid and believed that this fraction of K was in the chemical form of potassium silicate.

It is seen in Table 2 that only a small fraction of the AAEM species in the ash obtained in the rice straw combustion experiments at 1173 K were water-soluble. In addition, most of the AAEM species in the ash could not be dissolved in 1% HNO_3 , as presented in Table 4. Therefore, it is supposed that most of the AAEM species in the ash were in the chemical form of silicate.

This was supported by the elemental analysis and the SEM–EDX analysis of the ash obtained in the rice straw combustion experiment at 1173 K, as presented in Table 5 and Figure 4.

Table 5. Elemental Composition and the Content of Main Ash-Forming Elements in the Ash (1173 K) (wt %)

C	0.30
H	0.02
N	0.00
O (by difference)	44.90
Ca	3.98
Fe	0.88
K	10.07
Mg	1.39
Na	0.42
P	0.84
Si	37.19

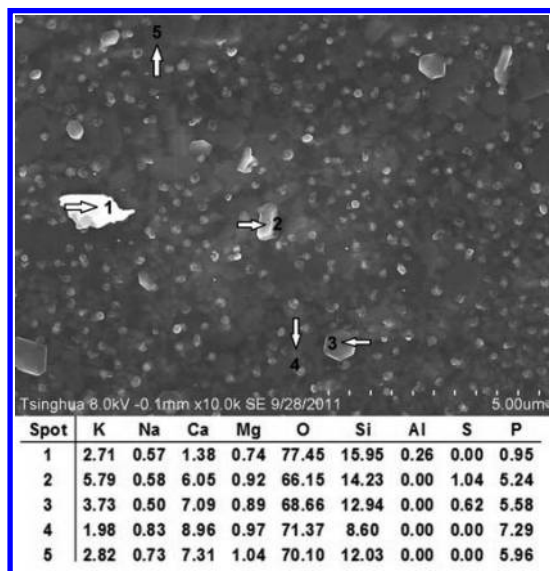


Figure 4. SEM micrograph and EDX spot analysis (value in mol %, C-free) of the ash obtained in the rice straw combustion experiment at 1173 K.

It is seen in Table 5 that the Si content in the ash was 37.19 wt %. Meanwhile, according to the SEM–EDX spot analysis in Figure 4, the AAEM species, Si, and P were widely distributed around the ash surface, indicating that the AAEM species were generally binding to silicate and phosphate in the ash. Lindstrom et al.⁸ also reported that the silicate and phosphate of the AAEM species existed in the bottom ash of the cereal grains during the combustion process. Because the P content in the ash obtained in the rice straw combustion experiment at 1173 K was much less than that of Si, as presented in Table 5,

it indicated that most of the AAEM species were binding to silicate in the ash and the AAEM species in the phosphate only covered a small fraction.

The morphology and elemental association of the AAEM species in the collected particles on quartz filter 2 obtained in rice straw pyrolysis and combustion experiments at 1173 K were studied using SEM–EDX analysis, as shown in Figure 5.

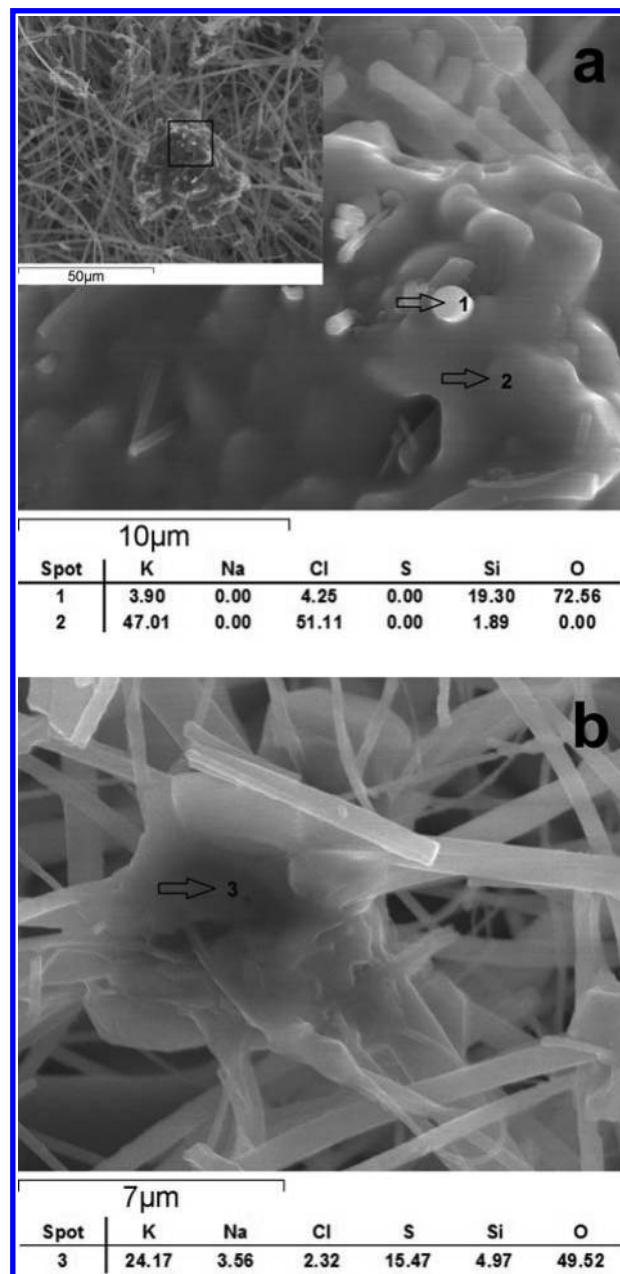


Figure 5. SEM micrograph and EDX spot analysis (value in mol %, C-free) of the collected particles on quartz filter 2 in the (a) rice straw pyrolysis experiment and (b) rice straw combustion experiment at 1173 K.

It is seen from Figure 5a that K and Cl were the major elements of the particles collected on the quartz filter 2 in the rice straw pyrolysis experiment at 1173 K. The white spot that was shown in Figure 5a in position 1 was the quartz fiber. In Figure 5b, K, Na, Cl, S, Si, and O were found in the particles collected on the quartz filter 2 that were obtained in the rice straw combustion experiment at 1173 K.

The chemical form of the particles collected on the quartz filter 2 was also analyzed by the water leaching experiment. The IC analysis of the washing water of the filter showed that the anion was only Cl^- for the filter obtained in the rice straw pyrolysis experiment and the anions were Cl^- and SO_4^{2-} for the filter obtained in the rice straw combustion experiment.

Considering that Na and K were found in these particles collected on quartz filter 2 and Ca and Mg were not, as presented in Figure 2, it indicated that KCl and NaCl existed in the condensed particles collected on quartz filter 2 obtained in the rice straw pyrolysis experiment at 1173 K and KCl, NaCl, K_2SO_4 , and Na_2SO_4 existed in the condensed particles on quartz filter 2 obtained in the rice straw combustion experiment at 1173 K.

4. DISCUSSION

4.1. Influence of the Atmosphere on K Transformation. From Tables 2–4, it can be seen that 80% K in the char of the rice straw was water-soluble and mainly existed in the chemical form of carbonate and 9% K in the char was supposed to be binding to silicate. There was still 11% K in char that we do not know its chemical form. It is supposed that this fraction of K in the char of the rice straw was associated with the oxygen groups in the organic char matrix (designated as char K hereafter), because it is reported that the char K was not water-soluble and could be dissolved in the ammonium acetate or acid solution.⁹ For the ash, it can also be seen from Table 4 that 89% K in the ash was binding to silicate. Therefore, it can clearly be seen that, when the atmosphere changed from inert to oxidizing, the fraction of K in the chemical form of potassium silicate in the solid residue significantly increased, indicating that the reaction between K and the silicate matrix in the solid phase was greatly facilitated by the oxidizing atmosphere at 1173 K.

One explanation of this phenomenon was proposed by Knudsen et al.^{6,7} that the incorporation of K into silicate was possibly hindered by the organic material in the char and reactions between them would take place only after better contact was established. Because, in the oxidizing atmosphere, the porous char matrix of the rice straw would be oxidized and completely destructed, which was proven by the 0.3 wt % C content in the ash in Table 5, it is believed that the explanation proposed by Knudsen et al.^{6,7} was acceptable in this study.

When the K release in the rice straw combustion and rice straw pyrolysis experiments is compared in Figure 3a, it is seen that the K release was facilitated by the oxidizing atmosphere at 1073, 1173, and 1273 K. Considering the similarities of the atmosphere and thermal conditions in the devolatilization stage of both experiments, if there was any K released in this stage, the release amount of K in the devolatilization stage in both experiments would be the same. Besides, it is proven that most K in the ash existed in the chemical form of silicate that was unlikely to evaporate in the temperature from 1073 to 1273 K.^{6,9,17} Therefore, it could be confirmed that the K release during the ash stage of the rice straw combustion only covered a little fraction of the total K release in the rice straw combustion experiment at 1073, 1173, and 1273 K. Therefore, it could be concluded that the K release in the char combustion stage in the rice straw combustion experiment was higher than that in the post-devolatilization stage in the rice straw pyrolysis experiment from 1073 to 1273 K.

The K in the char mainly existed in the chemical form of K_2CO_3 and char K, as discussed above, and it was reported that gaseous atomic K, which will generally react further with H_2O

and form gaseous KOH, would be released from them through thermal decomposition in the biomass pyrolysis process.^{6,9,18} When the atmosphere changed from inert to oxidizing, H_2O would be generated by the oxidation of H in the char structure and H_2O will significantly decrease the stability of K_2CO_3 , resulting in a formation of gaseous KOH.⁶ For char K, because the char organic matrix would be destructed completely in the rice straw combustion experiment, as discussed above, the chemical structure of char K would also be destructed and K dissociated from char K was probably binding to other species. In such an oxidizing atmosphere, the oxide of K might form and further react with H_2O to form gaseous KOH with a high possibility. Considering that only partial thermal decomposition of the char K took place in the pyrolysis condition, the release of K from char K will be facilitated by the complete oxidation of the char organic matrix in the oxidizing atmosphere. Thus, because of the facilitation of the dissociation of K_2CO_3 and char K in the oxidizing atmosphere, the release of K during the char combustion stage in the rice straw combustion experiment was expected to be higher than that during the post-devolatilization stage in the rice straw pyrolysis experiment at 1073, 1173, and 1273 K.

It should also be noted that the facilitation of the reaction between K and silicate and that of the dissociation of K_2CO_3 and char K brought by the oxidizing atmosphere both took place at the char combustion stage in the rice straw combustion experiment at 1073, 1173, and 1273 K. Meanwhile, once K was incorporated into silicate, it would not release to the gas phase anymore. This suggested that a competition relationship existed between these two processes.

The K release data in the char combustion experiment at 1173 K (see Figure 3a) suggested that, even after a 1 h pyrolysis process, part of K_2CO_3 and char K in the char transformed and released to the gas phase when the atmosphere changed from inert to oxidizing. This further proved that an oxidizing atmosphere will facilitate the release of K from K_2CO_3 and char K in the char of the rice straw at 1173 K.

The SEM–EDX and water leaching analysis of the particles collected on quartz filter 2 in the rice straw pyrolysis and combustion experiments at 1173 K showed that KCl existed in these particles (see panels a and b of Figure 5). This was expected, because KCl was found to be one of the main chemical forms of K in the rice straw, as presented in Tables 2 and 3, and the vaporization of the KCl was a proven mechanism of K release during the pyrolysis and combustion of Cl-containing biomass when the temperature is near or above the melting point of KCl (1046 K).^{4,9} For K_2SO_4 found in the particles collected on the quartz filter 2 in the rice straw combustion experiment at 1173 K (see Figure 5b), it was supposed to be formed through chemical reactions of KCl, SO_2 , and O_2 ¹⁹ rather than vaporization and condensation of K_2SO_4 , because the evaporation rate of pure K_2SO_4 particles would be rather slow when the temperature is below 1273 K.⁶

4.2. Influence of the Atmosphere on Na Transformation. From Tables 2–4, it could be seen that 93% Na existed in the chemical form of Na_2CO_3 in the char and no Na in the char existed in the chemical form of silicate. The chemical form of the left part of Na in the char (7%) was supposed to be similar to K, namely, to be associated with the oxygen groups in the organic char matrix (designated as char Na hereafter). Also, 85% Na existed in the chemical form of silicate in the ash. These results indicated that the oxidizing

atmosphere also facilitated the reactions between Na and the silicate matrix in the rice straw at 1173 K.

Different from K, when the release data of Na in the rice straw combustion experiment are compared to those in the rice straw pyrolysis experiment in Figure 3b, it is seen that the oxidizing atmosphere suppressed the Na release from the rice straw at 1073, 1173, and 1273 K. Furthermore, it could be further analyzed that such suppression took place during the char combustion stage of the rice straw combustion experiment, as analyzed for the case of K.

It was discussed above that, in the char, Na mainly existed in the chemical form of Na_2CO_3 and char Na. It was also reported that Na_2CO_3 and char Na may be thermally decomposed in the pyrolysis condition and form gaseous atomic Na, which would further react with H_2O to form gaseous NaOH.^{5,9,20} As discussed in the case of K, in the char combustion stage of the rice straw combustion experiment, H_2O was formed and the char matrix was completely oxidized. These would also facilitate the release of Na from Na_2CO_3 and char Na in the char of the rice straw. However, according to the Na release data in the rice straw combustion experiment, it is seen that such facilitation was not observed at all and even some part of Na in the char, which originally could be released to the gas phase by thermal decomposition from Na_2CO_3 and char Na in the rice straw pyrolysis experiment, was retained in the solid phase in the rice straw combustion experiment at 1073, 1173, and 1273 K. Considering that the reactions between Na and silicate were also facilitated during the char combustion stage of the rice straw combustion experiment at 1173 K and nearly all Na in the ash existed in the chemical form of silicate, it indicated that a high fraction of Na_2CO_3 and char Na in the char reacted with silicate and finally resulted in a lower release of Na in the char combustion stage of the rice straw combustion experiment at 1073, 1173, and 1273 K.

This also indicated that Na was more favored to react with silicate than K during the char combustion stage of the rice straw combustion experiment at 1073, 1173, and 1273 K. Such a phenomenon could be explained by the experimental evidence provided by Gallagher,²¹ who suggested that NaCl can allow for K release from potassium silicate at 1073 K according to bench-scale experiments. Briefly, when the chemical interactions between NaCl and potassium silicate occurred, Na would substitute K from the potassium silicate and form sodium silicate. This means that the chemical affinity of Na with silicate was greater than that of K with silicate, which can explain the higher fraction of Na that transformed into silicate.

The Na release in the char combustion experiment at 1173 K (see Figure 3b) showed that no additional release of Na was observed in comparison to the release of Na in the rice straw pyrolysis experiment at 1173 K and further proved that the reaction between Na and silicate in the char was greatly promoted when the atmosphere changed from inert to oxidizing.

Similar to KCl, NaCl was also found in the particles collected on the quartz filter 2 in both rice straw combustion and pyrolysis experiments at 1173 K. The vaporization of NaCl was reported to be a possible release mechanism of Na from biomass when the temperature was above its melting point (1077 K);⁹ therefore, the existence of NaCl in the particles collected on quartz filter 2 in the rice straw combustion and pyrolysis experiments was also expected. For Na_2SO_4 that was found in the particles collected on the quartz filter 2 in the rice straw combustion experiment at 1173 K, it was also considered to be formed through chemical reactions of NaCl, SO_2 , and O_2 rather

than vaporization and condensation of Na_2SO_4 , because decomposition of Na_2SO_4 was considered to take place below 1173 K.^{22,23}

4.3. Influence of the Atmosphere on Ca and Mg Transformation. From Tables 2–4, it is seen that only 6% Ca in the char was water-soluble and 30% Ca existed in the chemical form of silicate in the char. Mg possessed a similar chemical form to Ca in the char. This indicated that more than 60% Ca and Mg in the char may exist in the chemical form of carbonate, phosphate, or sulfate or be organically associated with the char matrix (designated as char Ca and char Mg hereafter), which all could be dissolved in 1% HNO_3 but are not water-soluble. It is also seen that the fraction of Ca and Mg that was in the chemical form of silicate in the char and ash of the rice straw increased from ~30 to 81 and 95%, respectively, when the atmosphere changed from inert to oxidizing. This indicated that the oxidizing atmosphere facilitated the reactions between Ca and Mg and silicate in the rice straw at 1173 K.

It is also seen from Table 4 that the fractions of Ca and Mg that were binding to silicate in the char (1173 K) were higher than those of K and Na. In a thermodynamic sense, the formation of Ca/Mg silicates was much more favorable than that of potassium silicate.¹⁰ This may be responsible for a higher fraction of Ca/Mg silicates than K/Na silicates in the char of the rice straw.

When the release of Ca and Mg in the rice straw combustion experiment was compared to that in the rice straw pyrolysis experiment in panels c and d of Figure 3, it is seen that the oxidizing atmosphere suppressed their release at 1073, 1173, and 1273 K. As discussed for the case of K and Na, it is considered that the release of Ca and Mg during the char combustion stage of the rice straw combustion experiment was less than their release in the post-devolatilization stage of the rice straw pyrolysis experiment at 1073, 1173, and 1273 K.

Different from the carbonate of K and Na, the thermal decomposition of the carbonate of Ca and Mg in the temperature range from 1073 to 1273 K was not supposed to result in any release of Ca and Mg in the post-devolatilization stage of the rice straw pyrolysis experiment, because the products of their decomposition would be the oxide of Ca and Mg, whose melting points were much higher than 1273 K. Thus, it is supposed that the release of Ca and Mg in the post-devolatilization stage of the rice straw pyrolysis experiment mainly came from the thermal decomposition of char Ca and char Mg in the char of the rice straw in the temperature range from 1073 to 1273 K. This possible Ca and Mg release mechanism was reported before by Okuno et al.¹⁰ in the biomass pyrolysis process and by Quyn et al.²⁴ in the coal pyrolysis process.

For the char Ca and char Mg formed in the char of the rice straw, complete oxidation was also expected to occur on them in the oxidizing atmosphere at 1073, 1173, and 1273 K, as discussed for char K and char Na, and the oxide of Ca and Mg was also expected to form. However, this clearly would not facilitate the release of Ca and Mg, because the oxide of Ca and Mg will not release to the gas phase. Therefore, if the release of Ca and Mg in the post-devolatilization stage of the rice straw pyrolysis experiment mainly came from the thermal decomposition of char Ca and char Mg in the char, it can be concluded that their release will be suppressed when the atmosphere changed to oxidizing. This may partly explain why less Ca and Mg were released in the char combustion stage of the rice straw combustion experiment than in the post-devolatilization stage of the rice straw pyrolysis experiment at 1073, 1173, and 1273 K.

In panels c and d of Figure 3, it is also seen that the Ca and Mg release in the char combustion experiment was less than their release in the rice straw pyrolysis experiment at 1173 K. This was not expected, because the released Ca and Mg were not considered to be able to come back to the solid residue after the pyrolysis process in the char combustion experiment at 1173 K. Considering the standard deviation of the release of Ca and Mg, it is believed that this was attributed to the error of their release quantification. However, it still proved that no additional Ca and Mg release will be caused by changing the atmosphere from inert to oxidizing and further supported the suppression effect on the release of Ca and Mg of the oxidizing atmosphere discussed above.

5. CONCLUSION

The influence of the atmosphere on the transformation of the AAEM species during rice straw thermal conversion was studied by a fixed-bed reactor at 1073, 1173, and 1273 K. Two types of atmospheres were considered: 100% (v/v) N₂ to simulate pyrolysis and 1% (v/v) O₂ in N₂ balance to simulate combustion. The experimental results revealed that the atmosphere significantly influenced the transformation of the AAEM species in the rice straw during the thermal conversion process, and the following conclusions have been drawn: (1) When the release of the AAEM species in the rice straw pyrolysis experiment at 1073, 1173, and 1273 K was compared, the oxidizing atmosphere in the rice straw combustion experiment facilitated the release of K but suppressed the release of Na, Ca, and Mg. (2) In the solid residue of the rice straw pyrolysis experiment at 1173 K, above 80% K and Na existed in the chemical form of carbonate and ~30% Ca and Mg existed in the chemical form of silicate. In the solid residue of the rice straw combustion experiment at 1173 K, above 80% of the AAEM species existed in the chemical form of silicate. (3) The facilitation of the oxidizing atmosphere on K release from rice straw was caused by its enhancing effect on the decomposition of K₂CO₃ and char K in the char. The suppression of the oxidizing atmosphere on Na release was attributed to the fact that a high fraction of Na in the char reacted with silicate in rice straw combustion experiment. For the suppression of the oxidizing atmosphere on the release of Ca and Mg, the inhibiting effect of the oxidizing atmosphere on the release of Ca and Mg from char Ca and char Mg in the char was supposed to be the prime cause.

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Notes

The authors declare no competing financial interest.

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