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Leaching of Alkali and Alkaline Earth Metallic Species from Rice Husk with Bio-oil from Its Pyrolysis

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ABSTRACT: Removal of alkali and alkaline earth metallic (AAEM) species, in particular, that of potassium, is an effective way to upgrade rice husk, because its combustion and gasification often suffer from the formation of potassium silicate with a low softening or fusion temperature. This work has been investigating the leaching of AAEM species with a bio-oil (BO) from the pyrolysis of the parent rice husk. The leaching with BO, which had a pH of 2.59, gave removal rates of K and Na equivalent to or higher than those with an aqueous solution of hydrogen chloride (HCl aqueous) or acetic acid (AcOH aqueous) at pH of 2. The leaching abilities of BO in terms of the removal rates of Mg and Ca were equivalent to HCl aqueous at pH 0 and AcOH aqueous at pH < 2, respectively. Such performances of BO arose from the presence of not only AcOH with a concentration of 6 wt % but also phenolic compounds (phenol, alkylphenols, and methoxyphenols). The phenols permeated into the organic matrix of the rice husk, forming hydrophobic interactions as well as hydrogen bonds with macromolecules, making the matrix more accessible to AcOH and water, and thereby promoting the leaching of organically bound AAEM species. The result of the leaching test with a simulated BO quantitatively demonstrated the role of the phenolic compounds as the leaching promoter.

1. INTRODUCTION

Rice husk and straw are the most abundant agricultural bioresources and often characterized by high contents of Si and K, which are 10−20 wt % (as SiO_2) and 0.2−2 wt % on a dry basis, respectively.[1−5] Si and K are transformed into K_2SiO_3 or other types of silicates at elevated temperatures, while silicates are also formed with the other AAEM species. The alkali silicates have a melting point temperature as low as 800 °C[6] and, therefore, bring about problems in operating combustion and gasification, such as slagging, fouling, and defluidization.[7−11] Thus, removal of AAEM species, in particular, that of K, prior to the combustion or gasification is an important pretreatment of the rice husk/straw. The removal of AAEM species is also attractive for using the rice husk/straw as feedstock of Si, SiC, or SiO_2,[12,13] because silicon atoms are already in excellent contact with the organic matrix, in other words, a carbonaceous one.[12]

Portions of AAEM species are leached into water,[14,15] but the water-soluble species account for no more than 30−80% of the total. Such limitation arises from the presence or abundance of organically bound species in forms of carboxylates[16,17] and inorganic minerals, of which leaching requires an acidic medium.[18,19] There have been reports on the removal of AAEM species from rice husk/straw with aqueous solutions of mineral acids, such as HCl[13,20,21] and H_2SO_4,[13,14,22] or organic acids, such as acetic acid.[23] Use of the mineral acid is not reasonable in practice, because carryover of Cl or S to the conversion can cause problems of erosion/corrosion of metals or emission of gases with environmental impact. Employment of organic acid is not necessarily feasible from an economical point of view.

Pyrolysis of biomass produces bio-oil (BO) that is often a homogeneous mixture of water and organic matter rich in acetic and other organic acids and non-acids.[24] Acidic aqueous solution is also produced by heat treatment of biomass in hot compressed water.[25,26] Those solutions have potentials as agents for leaching of AAEM species. Oudenhoven and co-workers[27] recently proposed an application of an acetic-acid-rich portion of BO from the pyrolysis of woody biomass for leaching of AAEM species prior to pyrolysis. They demonstrated removal of K and other AAEM species, resulting in the increase in the BO yield successfully. The abundance of organic acids, such as acetic acid, in BO is essential for its leaching ability. However, features of BO as a leaching agent have not yet been clarified. BO is a complex mixture of organic compounds, and it is reasonable to expect that some or many of such compounds, even non-acidic compounds, can play roles of promotion or inhibition of the leaching.

This work investigated the leaching of AAEM species from a rice husk with a BO from the pyrolysis of the same rice husk. The leaching ability of the BO was compared systematically to those of aqueous solutions of HCl and acetic acid with different pH values. Results of leaching tests and analyses showed a leaching capability of the BO. It was explained quantitatively on the basis of the chemical composition of the BO that contained leaching promoters as well as acetic acid.

2. EXPERIMENTAL SECTION

2.1. Materials. A type of organically produced Japanese rice husk was dried completely in air at 110 °C for 24 h. The dried rice husk (RH) was used for the pyrolysis without any further pretreatment. RH was also pulverized to sizes of 150−250 μm and then subjected to leaching tests. The C, H, and N contents of the dried rice husk were determined with an elemental analyzer (PerkinElmer, series II). The

contents of AAEM species were measured according to the following procedure. About 10 mg of the pulverized RH was ashed upon heating to 600 °C in air, while no ignition of the solid occurred. The resulting ash was digested in an aqueous solution of HF and HNO$_3$ (1:1, mol/mol) and then solidified by evaporation of the acids and water. The ash was dissolved in an aqueous solution of CH$_3$SO$_3$H and subjected to ion chromatography. Details of the procedure are found in the literature.[28,29] Table 1 shows the elemental composition of RH.

Table 1. Elemental Composition of RH

element	content (wt % daf RH)	element or ash	content (wt % dry RH)
C	44.97	ash	22.0
H	5.56	Na	0.052
N	0.55	K	0.553
O[a]	48.91	Mg	0.090
		Ca	0.212

[a]By difference.

2.2. Preparation of BO. RH was pyrolyzed in a horizontal screw-conveyer (auger) reactor, which is popular in the biomass pyrolysis, with a peak temperature of 500 °C. The details of the reactor are reported elsewhere.[30,31] The BO was condensed at the reactor downstream with a silica-fiber-made aerosol filter (180 °C) and three condensers (4, −40, and −70 °C, respectively) in series.[30] The procedure of the pyrolysis[30] enables the product recovery in a range of 99−101 wt % on the basis of feedstock. The product yields are shown in Table 2. The heavy and light oils were defined as the deposit on the

Table 2. Yields of Pyrolysis Products

product	yield (wt % RH)
char	43.2
light oil (BO)	33.6
heavy oil	6.0
gas	17.2

aerosol filter, and the mixture of organic material and water was collected in the condensers. The light oil consisted of organic matter (33 wt %) and water (67 wt %). The water content of the light oil was higher than those previously reported for BOs from the fast pyrolysis of rice husks in a fluidized bed.[32−34] Such a difference was primarily attributed to the fact that the present pyrolysis was performed with a heating rate as low as 6 °C/s,[30,31] which is general for the pyrolysis in auger-type pyrolyzers. A decreasing heating rate tends to increase water and char yields and promote dehydration condensation (i.e., cross-linking) in relation to bond breaking.[29] The light oil, the pH of which was 2.59, was used for the leaching without either dilution or enrichment. The light oil is hereafter referred to as BO. The composition of the organic portion of BO was analyzed by gas chromatography/mass spectrometry (GC/MS) on a PerkinElmer Clarus 680 that was equipped with a SQ 8S mass spectrometer. A type of capillary column (GL Science, Inc. TC-1701; length, 60 m; inner diameter, 0.25 mm) was used for the chromatography. GC/MS identified more than 20 major compounds and quantified 8 phenolic compounds. Table 3 shows the contents of the 8 phenolic compounds in BO. It was also confirmed that acetic acid was the most abundant and representative acid in BO. Its concentration was 6.0 wt % BO. Another acid, propionic acid, was detected by GC/MS, but its concentration was as low as ca. 0.1 wt %.

2.3. Leaching of AAEM Species. RH was subjected to leaching tests with BO, an aqueous solution of HCl (pH 0.0, 1.0, 2.0, or 3.0), another aqueous solution of acetic acid (AcOH; pH 1.8, 2.0, or 3.0), or deionized water. The pH of AcOH aqueous with the highest concentration of AcOH was not measured but was calculated as 1.8 because the concentration was as high as 58.4 wt %. The method of calculation is described in the Appendix. An aqueous solution of acetic acid and the 8 phenolic compounds contained in BO was also

Table 3. Contents of Organic Acids and Phenolic Compounds in BO

compound	content (wt % BO)
acetic acid	6.0
propionic acid	0.10
phenol	0.19
2-methoxyphenol	0.12
2-methylphenol	0.068
4-methylphenol	0.11
2-methoxy-4-methylphenol	0.068
4-ethylphenol	0.067
2-methoxy-4-ethylphenol	0.060
2,6-dimethylphenol	0.14

prepared at the same concentration as in BO and used for the leaching test as the simulated BO (SBO). The conditions for the leaching are listed in Table 4. In every test, RH was immersed in the liquid, and the

Table 4. Conditions for Leaching Tests

test ID	leaching agent	initial pH	time (h)	temperature (°C)	liquid/RH mass ratio
1	water	6.50	24	25	20
2	AcOH	1.8[a]	24	25	20
3	AcOH	2.00[b]	24	25	20
4	AcOH	3.00[b]	24	25	20
5	HCl	0.00[b]	24	25	20
6	HCl	1.00[b]	24	25	20
7	HCl	2.00[b]	24	25	20
8	HCl	3.00[b]	24	25	20
9	BO	2.59[b]	24	25	10
10	BO	2.59[b]	2, 4, 8, 12, or 24	25	20
11	SBO	2.33[b]	24	25	20

[a]Calculated from the concentration of AcOH or HCl. [b]Measured with an pH electrode.

resulting slurry was stirred continuously for a prescribed period. After the leaching, the slurry was separated into the liquid and solid by filtration. The solid (RH-L) was dried at ambient temperature for 96 h under reduced pressure well below 0.1 kPa. The contents of AAEM species remaining in the RH-L were determined in the same way as described above. The tests were repeated 3 times under the same conditions for confirming the reproducibility. The rate of removal of AAEM species is defined by the following equation:

$$removal\ rate\ (\%) = [1 - (amount\ of\ metallic\ species\ left\ in\ RH$$
$$after\ leaching\ (g/g\ of\ RH)/amount\ of$$
$$metallic\ species\ in\ RH\ before$$
$$leaching\ (g/g\ of\ RH))] \times 100$$

The standard deviation for the removal rate was well below 1% for every AAEM species.

It was found for the leaching with BO that its organic components (mainly phenolic and dehydrated sugars) had been retained in the RH-L. After drying at ambient temperature and pressure to avoid the release of the retained organic compounds, the RH-L was washed with methanol at 30 °C for 24 h to extract the retained compounds.

2.4. Stepwise Leaching for Classification of AAEM Species. The mode of occurrence of the AAEM species in the RH was investigated according to a known procedure.[35,36] RH was washed stepwise with deionized water (temperature, 25 °C; time, 24 h), a 1 M aqueous solution of ammonium acetate (25 °C, 24 h), and then a 1 M aqueous solution of HCl (80 °C, 48 h). The liquid/solid mass ratios were fixed at 20 for all of the steps. The contents of AAEM species in

the solid from each step were measured in the same way as described previously. Then, each K, Na, Ca, and Mg in RH was classified into water-soluble (WS), ammonium-acetate-soluble (AAS), HCl-soluble (HCS), and insoluble (IS) types. Two series of the stepwise leaching were performed with the same conditions and independently. The measured fractions for each type agreed with each other within an error smaller than 0.7%.

3. RESULTS AND DISCUSSION

3.1. Mode of Occurrence of AAEM Species in RH. Table 5 shows the fractions of WS, AAS, HCS, and IS for the

Table 5. Composition of AAEM Species in RH (wt %)

element	WS	AAS	HCS	IS	WS + AAS
Na	69.0	25.1	3.5	2.4	94.1
K	70.9	25.0	1.2	3.0	95.9
Mg	45.5	42.5	7.1	4.8	88.1
Ca	36.5	25.4	34.2	3.9	61.9

individual AAEM species. Na and K consist mainly of WS and AAS. These two types also represent the major portion of Mg, while it contains less of a portion of WS than the alkalis. The composition of Ca is clearly different from those of the other AAEM species. HCS accounts for about $^1/_3$ of the total content of Ca. It is believed from previous studies[37,38] that $CaCO_3$ and/or other mineral matters, such as Ca silicates, which are insoluble to either water or ammonium acetate solutions, contribute to Ca HCS. WS and AAS are reasonably attributed mainly to chlorides of AAEM species and organically bound species that are ion-exchanged to acidic oxygen functionalities, respectively.[35−38] The major portions of the AAEM species are leachable in the aqueous solution of HCl with pH 0. The chemical forms of IS are unknown, but a possible form is silicate.[35−38]

The fractions of WS, AAS, HCS, and IS of AAEM species should, in theory, be considered more carefully. Each step of leaching is performed in a batch system, which might allow for transformation of a type of AAEM species into another. The WS-to-AAS transformation is a possible example. AAEM species in a form of chloride is easily dissolved into water and then potentially associated with a carboxylic group (−COOH) through ion exchange. Once this WS-to-AAS transformation occurs, the newly formed AAS may not be leached with water. Therefore, the result in Table 5 might not directly show the modes of occurrence of AAEM species. This issue is, however, not discussed further in this report because the examination of the above-mentioned possibility is beyond the scope of the present study. Rather, the following discussion will be based on the modes of occurrence of AAEM species shown in Figure 1.

3.2. Combined Effects of Leaching Agent and pH on Removal Rates. Figure 1 shows the removal rates of the individual AAEM species as functions of the initial pH of the leaching agents, i.e., the aqueous solution of HCl (HCl aqueous), the aqueous solution of AcOH (AcOH aqueous), BO, and deionized water.

3.2.1. Removal Rates of K and Na. The K removal rate increases with the decrease in pH for both HCl aqueous and AcOH aqueous. Taking the abundances of WS, AAS, HCS, and IS in RH into consideration, the variation in the removal rate with pH at 1−3 has arisen from that of K−AAS, i.e., organically bound (ion-exchanged) K, and probably also the distribution of acidity (pK_a) of carboxyl groups. In general, lower pH is necessary to convert −COOM (M = K or Na) to −COOH that has a smaller pK_a. It is also seen in the figure that the K removal rate by the leaching with HCl aqueous at pH of 2−3 is lower than those by the leaching with AcOH aqueous. Assuming that the removal rate of K−AAS is determined by pH of the aqueous solution unless the accessibility of RH to the leaching agent is a controlling factor, the difference between HCl aqueous and AcOH aqueous suggests that K−AAS had better accessibility to AcOH aqueous than to HCl aqueous. The K removal rate with BO is slightly higher than that with AcOH aqueous, and it seems that the accessibility of K−AAS to BO is at least as good as to that to AcOH aqueous. The leaching with HCl aqueous and that with AcOH aqueous give almost
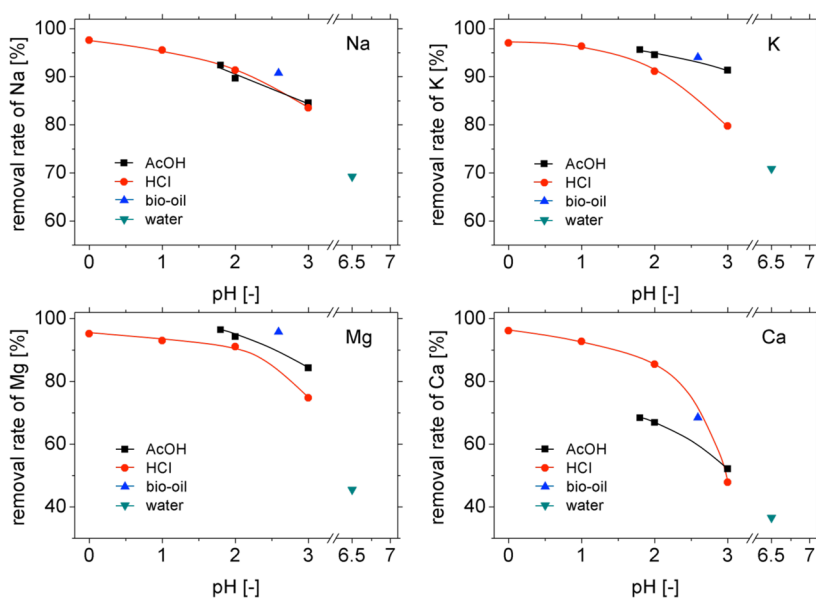

Figure 1. Removal rates of AAEM species for leaching with aqueous solution of AcOH, HCl BO, and water as a function of the initial pH. The liquid/solid mass ratios were 20 for all of the conditions.

equivalent removal rates of K at pH 1.8. Such little or no effect of the leaching agent on the removal rate is explained by equivalent accessibility of RH to these agents. It was found at pH 1 that small portions of RH, ca. 6 wt %, were dissolved into both HCl aqueous and AcOH aqueous. Although not investigated in detail, it was believed that a portion of carbohydrate underwent acid-catalyzed hydrolysis.[23] This could enhance the accessibility of RH to the leaching agents, creating their pathways to K−AAS. The Na removal rate by the AcOH leaching is near equivalent to that by the HCl leaching at equivalent pH. A comparison of the leaching agent effects on the removal rates of K and Na leads to an idea that Na−AAS is more accessible to the aqueous liquid than K−AAS. It is also noted that the BO leaching gives a higher removal rate than those with HCl aqueous and BO at the same pH. The accessibility of Na−AAS to BO seems to be better than that to HCl aqueous and AcOH aqueous.

3.2.2. Removal of Mg and Ca. The Mg removal rate by the BO leaching is 96%, and it is equivalent to the total fraction of Mg−WS, Mg−AAS, and Mg−HCS. This removal rate is as high as that by the AcOH leaching at pH 1.8 and even higher than that by the HCl leaching at pH 1. Such extensive Mg removal by the BO leaching is explainable by more capability of BO to reach the soluble Mg than that of AcOH aqueous as well as HCl aqueous. The Ca removal rate by the BO leaching is 70%, and it is as high as that by the AcOH leaching at pH 1.8. The removal rate, 70%, is slightly higher than the total fraction of Ca−WS and Ca−AAS, which is 62%. A portion of Ca−HCS can thus be dissolved into BO. It is, however, unable to remove a major portion of Ca−HCS, which is removed by the HCl leaching at pH 1 or lower.

The Ca removal by the AcOH leaching is around 70% at pH 1.8−2. This indicates the presence of Ca species (ca. 30% of the total Ca) that are insoluble to AcOH aqueous even at a high concentration. As discussed above, the accessibility of K and Na to AcOH aqueous as well as to BO is better than that to HCl aqueous. The HCl leaching, nonetheless, gives a clearly higher Ca removal rate than the AcOH leaching. This is not explainable by assuming that Ca−HCS consists mainly of $CaCO_3$, because its solubilities to AcOH aqueous and HCl aqueous are both much greater than the measured solubility of Ca in the RH under the present conditions.[39,40] It is therefore believed that the major portion of Ca−HCS in the RH is in the form of Ca silicates and/or others that are hardly soluble or insoluble to aqueous solutions of organic acids.[12,14] Thus, the Ca removal rate over 70% does not necessarily require permeability and/or accessibility of the organic/inorganic matrix of RH to the leaching agent but may need a particular type of acid, such as HCl.

The data in Figure 1 demonstrate that, at pH 2.59, BO removes more amounts of K, Na, and Mg than HCl aqueous and also more amounts of Na, Mg, and Ca than AcOH aqueous. It is reasonable to say that such better performances of the BO leaching are attributed to excellent affinity of BO with the matrix of the RH. However, this cannot be explained by the abundance of AcOH in BO alone. It is suggested that other components of BO promoted the access of AcOH to AAEM species in RH.

3.3. Kinetics of Leaching with BO. Figure 2 shows changes in the removal rates of AAEM species with leaching time. The removal rates of K, Na, and Ca level off within 2 h. The Ca removal rates increase more slowly. After 4 h, at which the removal rate reaches 62%, removing Ca−WS and Ca−AAS
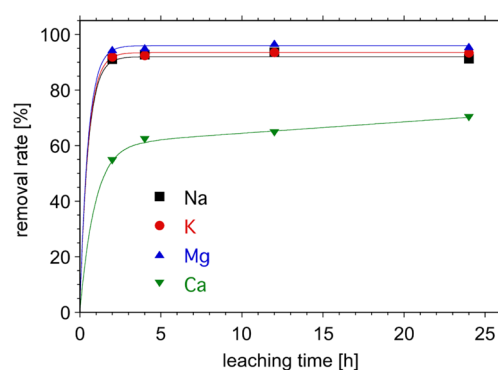

Figure 2. Time-dependent changes in removal rates of AAEM species during leaching with BO. BO/RH mass ratio = 20.

completely, leaching of Ca (i.e., that of Ca−HCS) occurs very slowly.

3.4. Examination of the Role of Phenolic Compounds as a Permeation Promoter. If some or many components of BO behaved as leaching promoters, they would be sorbed (adsorbed and/or absorbed) to the organic matrix of RH with the occurrence of hydrophilic or hydrophobic molecular interaction. With such an expectation, RH-L from the BO leaching was subjected to extraction with methanol, and the extract was analyzed by the GC/MS. The period of leaching was varied over the range from 2 to 24 h, while the BO/RH mass ratios were fixed at 20. Figure 3 displays a GC/MS
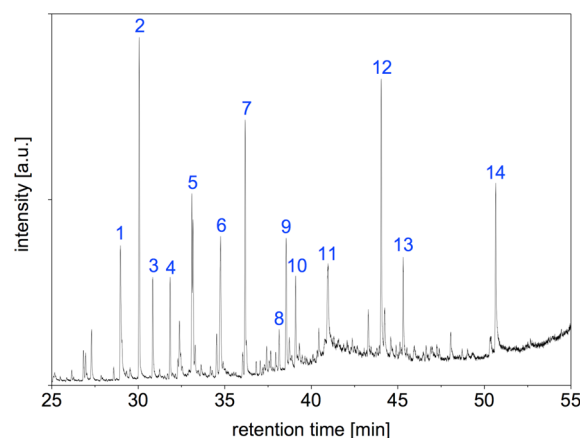

Figure 3. GC/MS chromatogram of the methanol extract from RH after BO leaching for 12 h at a BO/RH mass ratio of 20. Compounds: (1) 1,2-cyclopentanedione, 3-methyl-, (2) phenol, (3) phenol, 2-methoxy-, (4) phenol, 2-methyl-, (5) phenol, 4-methyl-, (6) phenol, 2-methoxy-4-methyl-, (7) phenol, 4-ethyl-, (8) phenol, 4-ethyl-2-methoxy-, (9) 1,4:3,6-dianhydro-α-D-glucopyranose, (10) benzofuran, 2,3-dihydro-, (11) phenol, 2,6-dimethyl-, (12) hydroquinone, (13) 1,4-benzenediol, 2-methyl-, and (14) levoglucosan.

chromatogram of the methanol extract from a RH-L after the BO leaching for 12 h. The abundance of phenolic compounds provide evidence of their sorption to the matrix of RH. Other types of compounds, such as sugars, furans, and dihydroxybenzenes, were also found in the extract.

Figure 4 shows the time-dependent changes in the uptake of the 8 phenolic compounds. A common trend among these compounds is quick uptake within the initial 2 h. It is also seen that the sorbed amounts of phenol and 4-methylphenol increase again at 8−12 h, at which those of the other
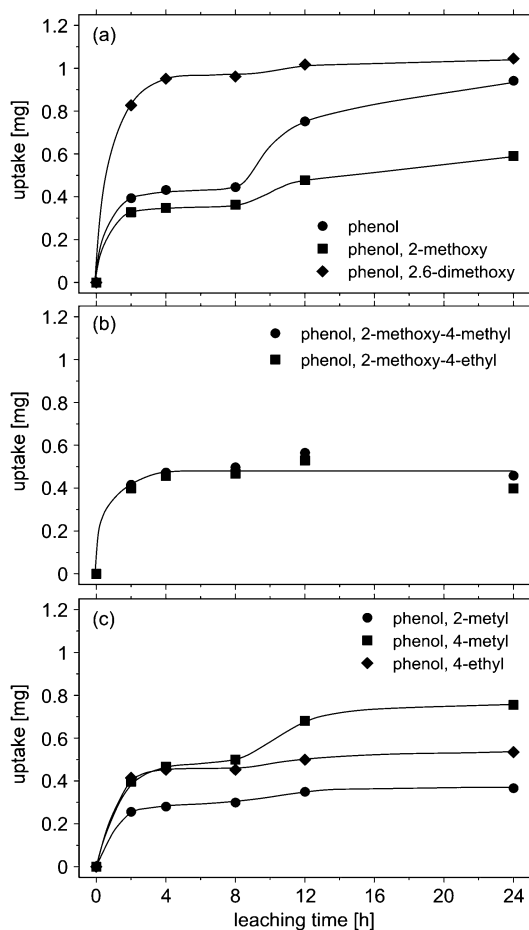
Figure 4. Time-dependent changes in the uptake of phenolic compounds by RH during BO leaching. The mass ratio of BO/RH was 20, regardless of the leaching period. (a) Phenol, 2-methoxyphenol, and 2,6-dimethoxyphenol, (b) 2-methoxy-4-methyl-phenol and 2-methoxy-4-ethylphenol, and (c) 2-methylphenol, 4-methylphenol, and 4-ethylphenol.

compounds increase but less extensively. The total uptake of the 8 compounds at 24 h was ca. 1.0 wt % RH (5.1 mg/500 mg of RH; Table 6). This corresponds to 6.1 wt % of the initial

Table 6. Uptake of Phenolic Compounds by RH at a BO/RH Mass Ratio of 20^a

compound	uptake (mg)
phenol	0.94
2-methoxyphenol	0.59
2-methylphenol	0.37
4-methylphenol	0.75
2-methoxy-4-methylphenol	0.47
4-ethylphenol	0.53
2-methoxy-4-ethylphenol	0.40
2,6-dimethylphenol	1.05

^{a}Mass of RH used for the leaching = 500 mg.

total content of the 8 compounds in BO. The quick uptake in the initial 2 h seems to be consistent with the rapid removal of AAEM species in the same period, which was long enough for the removal rate to reach the maximum. In other words, further uptake of the phenolic compounds was ineffective for increasing the removal rate.

Figure 5 illustrates a relationship between the fractional amounts of the individual compounds sorbed by RH from BO
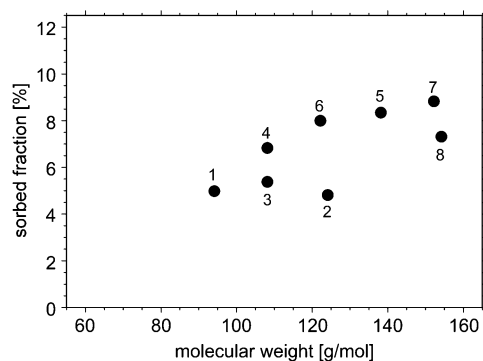

Figure 5. Fraction of phenolic compounds sorbed by RH as a function of the molecular weight. The phenolic compounds were extracted with methanol from RH after leaching with time and BO/RH mass ratio of 24 h and 20, respectively. Compounds: (1) phenol, (2) 2-methoxyphenol, (3) 2-methylphenol, (4) 4-methylphenol, (5) 2-methoxy-4-methylphenol, (6) 4-ethylphenol, (7) 2-methoxy-4-ethyl-phenol, and (8) 2,6-dimethoxyphenol.

and their molecular weights. The fractional amount corresponds to the partition coefficient under an assumption that the sorption reached near equilibrium or equilibrium within 24 h. The amount is correlated roughly with the molecular weight, and this indicates the importance of the hydrophobic interaction between the phenolic compounds and RH. Although not shown in the figure, the fractional amount was also correlated with the carbon atom number per molecule rather than that of oxygen atom number. These two correlations are consistent with each other. The hydrophobic interaction between the phenolic compounds and RH reasonably explains their roles of promoting the leaching. The permeation of phenols into the hydrophobic matrix of RH created pathways for AcOH as well as water molecules, which interacted well with hydroxyl and/or methoxy groups. It is also suggested that the phenolic compounds interacted with polar functionalities of RH, forming hydrogen bonds. Breakage of original hydrogen bonds inside the RH matrix would cause the swelling,[41−43] which was evidenced by the sorption of phenolic compounds under the present conditions.

The discussion developed above provides a reasonable explanation of the roles of the phenolic compounds as leaching promoters. The explanation was, however, a hypothesis. It was therefore necessary to prove the promotion of AcOH leaching by the phenolic compounds. An aqueous solution of AcOH was prepared and used for the leaching. It contained the 8 phenolic compounds as well as AcOH with the same concentrations as those in BO (see Table 3). This solution is hereafter referred to as the simulated BO or SBO.

SBO had a pH of 2.33, which was lower than that of BO, i.e., 2.59. A possible reason for such a difference in pH is evolution of acetates, such as AcOK and AcONa, together with AcOH during the pyrolysis and their condensation in BO.[44] Simple calculation was made assuming the followings: dissolution of AcOH and AcOM (M = K or Na) into pure water at a ratio of $[M^+]/([AcO^-] + [AcOH]) = \alpha$; total concentration of AcO, 6 wt % (ca. 1 mol/L), pK_a of AcOH, 4.75;[45] and ionic product of pure water, $10^{-14.0}$. The calculation predicted that pH values of the resulting solutions were 2.38 and 2.59 at $\alpha = 0$ and 0.0042, respectively. Thus, the pH of BO was sensitive to the

abundance of AAEM species that had been volatilized as acetates. Although it was difficult to determine α experimentally, volatilization of K and Na in the form of acetate salt is plausible.[46] Another possibility is the change in pK_a of AcOH because of the presence of phenolic compounds and other organic components of BO. It was found that the addition of the phenolic compounds to AcOH aqueous increased pH slightly, i.e., from 2.31 to 2.33. Interaction between acetate ions (AcO^-) and the phenols thus seemed to increase pK_a of AcOH. Such a change in pH is explained by solvation of acetate ions by the phenols via hydrogen bonds, which increases pK_a.[47] Taking the abundance of organic compounds that were capable of forming hydrogen bonds in BO into consideration, pH of BO as high as 2.59 is explainable.

Figure 6 shows that the removal rates of AAEM species by the leaching with SBO are almost equivalent to the respective
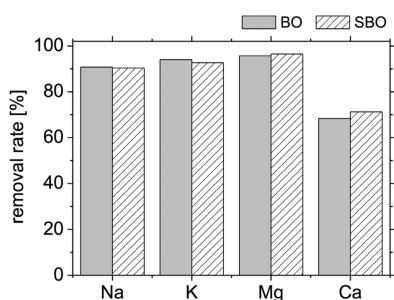

Figure 6. Removal rates of AAEM species by leaching with BO and SBO. BO/RH and SBO/RH mass ratios, 20; leaching time, 24 h.

rates by that with BO. It is thus demonstrated that the phenolic compounds promote the leaching of AAEM species by AcOH aqueous, in particular, that of Mg and Ca. This result does not necessarily mean that the phenolic compounds are the only leaching promoters in BO. In other words, contribution of other types of components is not eliminated. However, the leaching ability of BO is explainable only by the presence of the phenolic compounds. It is also seen that the Mg and Ca removal rates with SBO are slightly higher than those with BO, while the differences are ca. 1 and 2.5%, respectively. Such differences are explainable by the higher pH of SBO than BO. As seen in Figure 1, the removal rates of Mg and Ca with AcOH aqueous change with pH. According to the solid lines drawn in the graphs, decreasing pH from 2.59 to 2.33 results in inceasing the Mg and Ca removal rates by 2 and 2.5%, respectively.

3.5. Consideration of the Practical Use of BO for the Removal of AAEM Species. The discussion through the previous sections shows that the leaching ability of BO is based on the presence of AcOH and, additionally, that of leaching promoters. The applicability of BO to a practical leaching process is discussed here. Table 7 compares the removal rates

Table 7. Removal Rates of AAEM Species by BO Leaching at Different BO/RH Mass Ratios[a]

	removal rate (%)			
BO/RH mass ratio	K	Na	Ca	Mg
10	92.3	89.1	63.7	93.6
20	94.0	90.8	68.4	95.7

[a]Leaching time = 24 h.

of AAEM species by the BO leaching at BO/RH mass ratios of 10 and 20. The decrease in the mass ratio results in slightly but systematically lower removal rates. This trend appears to be explained by consumption of the proton by removal of ion-exchanged AAEM species (AAS). However, net consumption of the proton was insignificant within the range of the conditions. The initial and final pH values were 2.59 and 2.59–2.60, respectively, for both BO/ratios. It was rather suggested that RH sorbed more amount of promoters per mass of BO at the higher BO/RH ratio, which has not been confirmed experimentally. In practical and repeated use of BO for the leaching, shortening the leaching time can minimize the loss of promoters from BO. As seen in Figure 2, the major part of leaching of AAEM species is completed within 2 h. On the other hand, Figure 4 shows that the sorption of the phenolic compounds continues until 24 h.

Figure 7 shows a schematic diagram of a process, which just provides an idea of upgrading and conversion of RH. The RH is
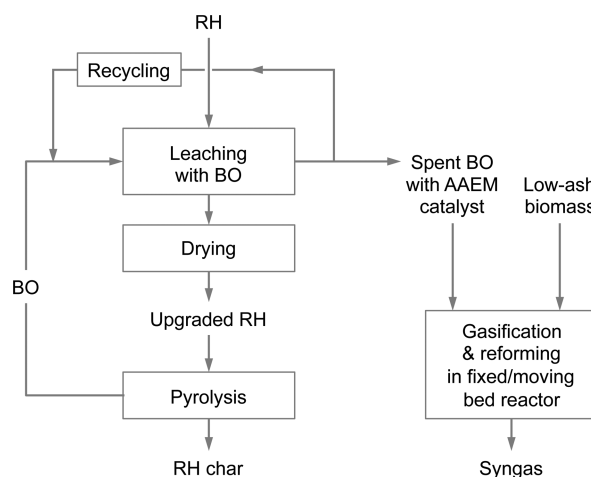

Figure 7. Process flow for upgrading and conversion of RH. The process consists of BO leaching, drying, pyrolysis (production of char and BO), and reforming of spent BO together with gasification of another type of biomass.

leached with BO, dried, and then pyrolyzed to BO and near-AAEM-free char. The BO is used for the leaching in a recycling mode, which is necessary to maintain a BO/RH mass ratio high enough for preparation of a slurry. The char is not only solid fuel but also a source of SiO_2 or reductant of Si. The spent BO consists of water, organic matter, and AAEM species, and it is therefore an excellent source of steam, volatile matter, and reforming/gasification catalyst, respectively. A reasonable way to use the spent BO is its co-gasification/reforming with low-ash biomass. In this process, RH-derived AAEM species will play catalytic roles after deposited onto char. Although not investigated in the present study, applicability of BO to repeated use for the leaching is a most critical factor in the design of processes, as illustrated in Figure 7.

4. CONCLUSION

The present work investigated the removal of AAEM species in the leaching of RH with HCl aqueous, AcOH aqueous, or BO. The following conclusions are drawn from the experimental and analytical results. The removal rates of Na, K, Mg, and Ca by the BO leaching are higher than rates by both the leaching with HCl and that with AcOH or either of them at the same pH

of 2.59. Such a performance of BO is explained by the presence of AcOH and, more importantly, by that of phenolic compounds as leaching promoters. The removal rates of the individual AAEM species by the BO leaching are experimentally and quantitatively simulated by SBO, which has the same contents of AcOH and the 8 different types of phenolic compounds as BO.

■ APPENDIX

The concentration of AcOH on an aqueous solution used in the present study was 9.99 mol of AcOH/L. It was out of range in which a general electrode is available in measuring pH. Then, pH of this solution was calculated applying the following equations:

definition of the equilibrium constant (K_a) of dissociation of AcOH

$$\frac{[\text{AcO}^-][\text{H}^+]}{[\text{AcOH}]} = K_a \quad (A1)$$

calculation of K_a from thermodynamic K_a (K_a°) and activity coefficients (γ)

$$pK_a = pK_a^\circ + \log \gamma_{\text{H}^+} + \log \gamma_{\text{AcO}^-} + \log \gamma_{\text{AcOH}}$$
$$(K_{a1}^\circ = 4.75) \quad (A2)$$

calculation of activity coefficients for H^+ and AcO^- by Davies equation[48]

$$\log \gamma_i = 0.5z_i^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.15I\right) \quad (A3)$$

where I is the ionic strength of the solution and z is the charge number of ionic species i

charge balance

$$[\text{H}^+] \approx [\text{AcO}^-] \quad (A4)$$

The four equations were solved simultaneously, assuming $\gamma_{\text{AcOH}} \approx 1$. Then, pH = $-\log(\gamma_{\text{H}^+}[\text{H}^+])$ = 1.8 was calculated.

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Notes
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