



Title	Effects of Ash Composition and Combustion Temperature on Reduced Particulate Matter Emission by Biomass Carbonization.
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1 **Effects of ash composition and combustion temperature on reduced particulate matter emission by**
2 **biomass carbonization**

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15 **Abstract**

16 Thermochemical pretreatment, including carbonization, has been suggested as a method to reduce
17 particulate matter (PM) emissions during the combustion of biomass. However, the carbonization efficiency
18 might not be equal for all types of biomass because of composition heterogeneity and differences in
19 combustion conditions. Therefore, an assessment of PM emission reduction by carbonization of various
20 types of biomass at different combustion temperatures is required. In this study, seven different types of
21 biomass (larch, poplar, miscanthus, bamboo grass, rice straw, rice husk, and dairy manure) and their
22 biochars (prepared at 400 °C) were combusted at 650, 750, and 850 °C. The results showed that PM
23 emission was reduced as much as 95.45% after carbonization as a result of volatile matter removal. The
24 efficiency of PM reduction was greatest at low combustion temperatures for all feedstocks. Although the
25 combustion temperatures did not strongly affect PM emissions from low-ash ($\leq 6.7\%$) biomass, higher

26 heating temperatures (≥ 750 °C) stimulated PM emissions from ash-rich rice straw and dairy manure biochar.
27 The transformation of minerals in rice straw, rice husk, and dairy manure was also investigated at different
28 combustion temperatures (650, 750, and 850 °C). Mineral analysis revealed that enhanced PM emission
29 from ash-rich biochar samples was attributable to a greater concentration of Na and K, which likely resulted
30 from melting at higher combustion temperatures. We found that carbonization can substantially reduce PM
31 emissions for low-alkali-containing biomass and that a lower combustion temperature of biochar is
32 preferable to suppress PM emissions for high-alkali-containing biomass. Our findings reveal a possible
33 approach to waste-to-energy production with reduced health risks.

34 **Keywords:** Biofuel, Pyrolysis, Fuel upgrading, Mineral content

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43

44 1. Introduction

45 Reducing dependency on fossil fuels is important because they are the main source of anthropogenic CO₂
46 emissions to the atmosphere, have limited future availability, and are nonrenewable. Therefore, biomass-
47 based solid biofuel is gaining popularity worldwide as a sustainable energy source [1]. Biomass fuel is
48 defined as plant- or animal-derived material used as a source of energy to generate electricity or heat.
49 Currently, approximately 3 billion people rely on solid bio-based fuels, such as wood, crop wastes, charcoal,
50 and dung, for their heating and cooking needs [2]. However, the traditional method of utilizing biomass in
51 rural areas is to fuel undeveloped stoves with raw biomass and coal, which has several drawbacks including
52 low energy density and the emission of unhealthy particulate matter (PM) during combustion [3–5].
53 Consequently, in developing countries, nearly 4 million premature deaths are caused by household air
54 pollution each year, mainly as a result of emissions from biomass combustion [6, 7]. Therefore, to improve
55 the energy density in biofuels and prevent indoor air pollution, technologies for improving biomass-based
56 fuels are critical.

57 To address the problems associated with solid biofuel, several pretreatment strategies, including
58 physical, chemical, thermophysical, thermochemical, and biological methods, have been examined [8, 9].
59 Among them, thermochemical pretreatment of biomass is attracting attention because of its simplicity and
60 effectiveness. This technology includes both torrefaction and carbonization, which partially decompose
61 biomass and produce carbonized biomass known as biochar via volatile matter (VM) reduction. These
62 methods have previously been observed to effectively increase the energy density in solid biofuels and
63 reduce PM emissions during combustion because of the decrease in VM [10, 11]. However, Itoh et al.
64 suggested that the reduction in PM emissions depends on both the reduction rate of VM and the type of
65 biomass used [11]. They also reported that torrefaction of dairy manure increased the ash content in the
66 resultant biochar, which decreased the overall efficiency of PM emission reduction compared with that
67 achieved using low-ash woody biochar [11].

68 Like dairy manure, numerous types of waste-derived biomass have a high ash content and are usually
69 considered low-grade biomass (LGB) [12]. PM emissions due to the enhanced ash content of the carbonized
70 biomass is a major concern when these LGBs are used as biofuel. Therefore, the mechanism of PM

71 emissions from biochar needs to be understood and methods to mitigate PM emissions should be developed.
72 Yang et al. have reported that variations in the inorganic-organic minerals of fuel ash influence the release
73 of PM. Specifically, some alkali-metals (e.g., K and Na) tend to contribute to PM emissions from biomass
74 and coal firing because they are easily volatilized [9]. The ash in LGBs is rich in alkali and, alkaline earth
75 metals (e.g., K, Na, Ca, Mg), and other minerals (e.g., Si, Al, P, Cl, and S), which are present in various
76 amounts depending on, for example, the biomass type, time of harvest, and the growing conditions [12].
77 To develop a method for PM reduction and evaluate the efficacy of carbonization, the effect of the ash
78 composition within different biomass types on PM emission should be clarified.

79 In addition, in most studies where PM emissions have been measured, combustion temperatures greater
80 than 1000 °C were used for either biomass or coal combustion [9]. However, in practical situations, stove-
81 bed temperatures range between 700 and 1000 °C during the char combustion phase, and even lower
82 temperatures have been observed during the ignition and flame phase [13]. Thus, given the boiling points
83 of K and Na (759 and 883 °C, respectively), testing the influence of different combustion temperatures on
84 PM emissions by comparing raw and carbonized biomass is necessary for evaluating the applicability in
85 real-world situations. However, the literature contains little research on the effects of biomass
86 compositional differences and combustion temperature variability on the potential reduction of PM
87 emissions by carbonization.

88 In the present work, to clarify the PM emissions from various types of biomass and their carbonized
89 products, and to propose a potential method for reducing PM emissions on the basis of ash content and
90 composition, we hypothesized that low combustion temperatures reduce the PM emissions from carbonized
91 biomass, even biomass with a high ash content.

92 **2. Materials and methods**

93 2.1. Materials

94 Fourteen samples (raw biomass and their biochar from seven different feedstocks) were used. Feedstocks
95 with different ash contents and resource availability were selected. Rice straw (RS), rice husk (RH), and
96 dairy manure (DM) are wastes generated from agriculture. Giant miscanthus (*Miscanthus giganteus*) (Mi)
97 is a short-rotation energy coppice, is abundant, and has a relatively low ash content. Poplar (*Poplar spp.*)

98 (Po) is a representative fast-growing forest coppice, and Japanese larch (*Larix kaempferi*) (JL) is an
99 abundant tree species of temperate forests. Woody biomass shavings are attractive because of their low ash
100 content. Bamboo grass (BG) from *Sasa kurilensis* is an invasive species in the temperate forest of northern
101 Japan. Removal of bamboo is an effective silvicultural method to sustain overstory plant diversity, but is
102 not widely utilized [14]. All raw biomass samples were collected from the experimental farm and campus
103 of Hokkaido University, Sapporo, Japan. The samples were dried at 105 °C for 24 h to remove inherent
104 moisture, then milled and sieved through a 0.5-mm sieve.

105 Biochar samples were produced by pyrolysis of the biomass at 400 °C for 1 h in a FO810 muffle furnace
106 (Yamato Scientific, Tokyo, Japan). Biochar samples were designated as RSB (rice straw biochar). A
107 pyrolysis temperature of 400 °C was selected on the basis of the high char yield and efficiency of VM
108 reduction at this temperature [11]. To determine minerals that could contribute to PM emissions, ash was
109 heated at different temperatures (650, 750, and 850 °C) using some high-ash (>10%) biomass (e.g., RH,
110 RS, and DM). The ash samples were prepared by incineration of the raw materials in a muffle furnace at
111 600 °C for 3 h and were subsequently stored under airtight conditions. After the samples were incinerated,
112 300 mg of each ash sample was heated at 650, 750, or 850 °C for 60 min in a tube furnace. The products
113 are referred to as heated ash samples.

114 2.2. Proximate and ultimate analyses

115 The VM content of raw and carbonized biomass was determined according to the method specified in
116 standard ASTM (i.e., heating the dried feedstock at 950 ± 20 °C for 7 min). For determination of the ash
117 content, samples were combusted at 600 °C for 3 h in a muffle furnace. The fixed carbon (FC) content was
118 calculated by the difference ($FC [\text{wt.}\%] = 100 - VM [\text{wt.}\%] - \text{ash} [\text{wt.}\%]$). The carbon, hydrogen, and
119 nitrogen contents of the samples were determined using a CE-440 elemental analyzer (Exeter Analytical,
120 North Chelmsford, MA, USA). The oxygen content was calculated by subtraction ($O [\%db.] = 100 - C$
121 $[\%db.] - H [\%db.] - N [\%db.] - \text{ash} [\%db.]$). The mineral (Al, Ca, K, Mg, Na, P, and Fe) concentrations
122 in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer,
123 Waltham, MA, USA). Before the analysis, samples were digested in an HNO₃-H₂O₂ system and the liquid

124 fraction was analyzed by ICP-MS. The solid fraction, which was dominated by crude silica [15], was
125 collected by filtration and then weighed after drying.

126 The biochar yield (BY [%]) and carbon yield (CY [%]) were calculated using the following equations:

$$127 \quad BY = \frac{m_{\text{biochar}}}{m_{\text{feedstock}}} \times 100$$

$$128 \quad CY = BY \left(\frac{C_{\text{biochar}}}{C_{\text{feedstock}}} \right)$$

129 where m and C represent the dry mass [kg] and the carbon content on a dry basis [%], respectively.

130 2.3. PM emission factor measurement

131 To compare the emissions of total suspended PM during combustion of the raw and carbonized materials,
132 the emission factor (EF) of total PM was determined. To assess the effect of the combustion temperature
133 on the total PM EF (mg/g-fuel), samples were combusted at 650, 750, and 850 °C in an ARF-30KC tube
134 furnace equipped with an HK01P-11 temperature controller, as described in the study of Itoh et al. [11],
135 except that we did not use a PM emission sensor. The airflow rate was set at 4 L/min using a mass flow
136 controller. When the temperature of the tube furnace reached the designated value, 500 ± 0.05 mg of sample
137 was weighed into a sample boat and introduced into the glass tube to combust for 60 min. Each experiment
138 was repeated three times at each temperature.

139 Total PM EF was determined by the weight difference of quartz-fiber filters (2500 QAT-UP, Tokyo
140 Dylec, Tokyo, Japan) before and after the experiment. Before the combustion experiment, the filters were
141 heated at 650 °C for 1 h to remove moisture and impurities and were then placed in a desiccator for 24 h at
142 room temperature prior to their weight being measured and recorded. After the samples weighed, the
143 reduction rate of PM EF was estimated by comparing the value of the raw and carbonized materials using
144 the method of Itoh et al. [11].

145 To compare the efficiency of pyrolysis for reducing PM emissions, the reduction rates of VM and PM
146 were calculated using the following equations.

$$147 \quad \text{Reduction rate}_{VM} (\%) = \left(1 - \frac{VM_{\text{biochar}}}{VM_{\text{feedstock}}} \right) \times 100$$

$$148 \quad \text{Reduction rate}_{PM} (\%) = \left(1 - \frac{PM_{\text{biochar}}}{PM_{\text{feedstock}}} \right) \times 100$$

149 where VM is the percentage of volatile matter (%) and PM is the total PM EF (mg/g-fuel) particulate matter
150 emitted from each raw biomass and biochar product.

151 2.4. Statistical analysis

152 To determine the difference among the treatments shown in Fig. 1 and Table 3, a one-way analysis of
153 variance (ANOVA) was conducted using the IBM SPSS (version 28) statistics program. Tukey's test was
154 used to determine if a significant difference ($p < 0.05$) existed in the PM emission factor (Fig. 1) analysis
155 within the same raw and carbonized material of each feedstock or in the K and Na content analysis (Table
156 3) in the ash and heated ash samples of the RH, RS, and DM. A correlation test between the PM emission
157 factor and the K and Na content in the biochar samples was conducted in MS Excel.

158 3. Results and Discussion

159 3.1. Fuel properties

160 3.1.1. Proximate analysis

161 The results of the proximate and ultimate analyses of all feedstock and biochar samples are summarized in
162 Table 1. The VM content in the raw materials was much greater than the FC and ash contents. The VM
163 content ranged between 71.0% and 88.7% and was greatest in the Po, JL, and Mi samples. Among the
164 biochar samples, the VM content varied from 22.3% to 43.4%, depending on the feedstock, and was
165 significantly lower than in the raw materials. For example, the VM content was the greatest in woody
166 biochars (JLB, PoB), followed by MiB and DMB, whereas RHB and BGB contained the smallest amount
167 of VM. The FC content in the raw samples was lowest in DM (10.5%) and greatest in Mi (16.9%). In the
168 biochar samples, the FC content varied significantly (27.5–61.4%) among the feedstocks and followed the
169 trend $DMB < RSB < RHB < JLB < PoB < MiB < BGB$. The ash content of the biomass also varied greatly
170 between 0.0% and 17.6%, depending on the biomass type. The ash content was greatest in agricultural
171 residues with DM (17.6%), RH (14.3%), and RS (12.2%), whereas the ash content of JL, Po, Mi, and BG
172 samples was relatively low (0.0–6.7%). According to Vassilev et al., the ash content of biomass decreases
173 in the order animal and human-derived biomass > herbaceous and agricultural biomass > woody biomass
174 [16]. The ash content based on biomass category in the present study was found to be consistent with that
175 reported in the literature. In the biochar samples, the ash content had a wide range (1.3–41.2%) and

176 increased in the order JLB < PoB < MiB < BGB < RSB < RHB < DMB. Because of pyrolysis, the ash
 177 content of the biochars produced from high-ash raw materials (RH, RS, DM) increased significantly,
 178 whereas the ash content in the other samples increased only slightly.

179 Table 1. Proximate and ultimate analysis of raw and carbonized biomass

Sample	Ultimate analysis (%db)				Proximate analysis (%db)		
	C	H	N	O	VM	FC	Ash
RH	38.9 ± 1.5	5.2 ± 0.4	0.5 ± 0.3	41.1 ± 2.1	71.0 ± 1.1	14.7 ± 1.1	14.3 ± 0.4
RS	38.7 ± 1.3	5.2 ± 0.1	0.5 ± 0.1	43.4 ± 1.4	73.6 ± 2.4	14.3 ± 2.4	12.2 ± 0.1
DM	42.2 ± 2.6	5.3 ± 0.3	1.7 ± 0.2	33.2 ± 2.7	71.9 ± 4.8	10.5 ± 4.8	17.6 ± 0.1
Mi	45.6 ± 0.0	5.6 ± 0.1	0.3 ± 0.0	45.4 ± 0.0	79.9 ± 5.7	16.9 ± 5.7	3.1 ± 0.2
Po	47.0 ± 0.4	5.8 ± 0.1	0.3 ± 0.0	46.3 ± 0.6	88.7 ± 0.3	10.8 ± 0.3	0.5 ± 0.4
JL	48.2 ± 0.4	5.8 ± 0.0	0.3 ± 0.0	45.7 ± 0.5	86.4 ± 0.6	13.6 ± 0.6	0.0 ± 0.0
BG	44.0 ± 0.2	5.6 ± 0.1	1.0 ± 0.2	42.7 ± 0.5	78.8 ± 0.4	14.5 ± 0.4	6.7 ± 0.1
RHB	50.1 ± 1.1	2.7 ± 0.0	1.1 ± 0.2	12.5 ± 1.3	23.4 ± 0.0	42.9 ± 0.0	33.7 ± 1.0
RSB	54.0 ± 1.6	2.8 ± 0.1	0.7 ± 0.0	13.6 ± 1.5	28.9 ± 0.8	42.1 ± 0.8	29.0 ± 0.5
DMB	45.3 ± 1.2	2.5 ± 0.2	2.3 ± 0.1	8.8 ± 1.5	31.3 ± 4.0	27.7 ± 4.0	41.2 ± 8.8
MiB	68.6 ± 0.5	3.2 ± 0.1	0.3 ± 0.0	20.2 ± 0.5	32.9 ± 1.2	59.4 ± 1.2	7.8 ± 0.2
PoB	71.5 ± 0.7	3.0 ± 0.1	0.3 ± 0.0	20.9 ± 0.7	39.1 ± 2.2	56.6 ± 2.2	4.2 ± 0.3
JLB	71.9 ± 0.6	2.8 ± 0.1	0.3 ± 0.0	23.7 ± 0.7	43.4 ± 0.6	55.3 ± 0.6	1.3 ± 0.1
BGB	61.6 ± 1.5	3.3 ± 0.3	1.3 ± 0.3	17.5 ± 1.5	22.3 ± 4.5	61.4 ± 4.5	16.3 ± 0.4

180 RH: rice husk; RS: rice straw; DM: dairy manure; Mi: Miscanthus; Po: Poplar; JL: Japanese larch; BG:
 181 bamboo grass; RHB: rice husk biochar

182 Overall, the increase in FC and ash content in biochar samples was due to VM release as a result of
 183 carbonization. The VM reduction rate (Table 2) due to carbonization was greatest in BG (71.70%) followed
 184 by RH, RS, Mi, DM, Po, and JL. Itoh et al. reported that woody biomass that contains less than 50% VM
 185 can be used to minimize PM emissions [11], suggesting that the risk of PM emission due to VM would be
 186 sufficiently reduced by the method proposed in the present study.

187 Table 2 Mass yield, carbon recovery, and VM reduction rate.

Biochar	MY (% db)	C recovery (% db)	VM reduction rate (% db)
Rice husk (RHB)	39.0	50.2	67.0
Rice straw (RSB)	41.9	58.4	60.7
Dairy manure (DMB)	31.0	31.0	56.5
Miscanthus (MiB)	33.1	49.8	58.8
Poplar (PoB)	36.7	55.8	55.9
Larch (JLB)	34.2	51.0	49.8
Bamboo grass (BGB)	36.3	50.8	71.7

188 MY: mass yield; VM: volatile matter; db: dry basis

189

190 *3.1.2. Ultimate analyses*

191 The ultimate analyses revealed that the C content of the raw materials ranged between 38.7% and
 192 48.2%, whereas that of the biochar samples was 45.3–71.9%. The least and greatest C-containing biomass
 193 samples were RS and JL, respectively. The recovery of C from each feedstock was calculated on the basis
 194 of the mass yield of the biochar (Table 2). All materials underwent C enrichment due to dehydration and
 195 decarboxylation during the pyrolysis process, and the yield was greatly influenced by the composition of
 196 the feedstocks. For instance, biomass with a high lignin content has been reported to yield more C in charred
 197 materials, whereas animal-manure- and sewage-sludge-derived biochar has been reported to yield less C
 198 than lignocellulosic biomass [17, 18]. Similar to the observation of Weber and Quicker [17], the C recovery
 199 of DM was the lowest in our study. C recovery from rice straw was greatest and was similar to that from
 200 the woody biomass (Po, JL), which is considered to have a relatively high lignin content compared with
 201 herbaceous biomass [5, 19].

202 The H content of raw biomass was between 5.2% and 5.8%, whereas that of biochar ranged from 2.5%
 203 to 3.3%. The N content in the raw and biochar samples ranged from 0.3% to 1.7% and from 0.3% to 2.3%,
 204 respectively. The O content in the raw material was lowest in DM (33.2%) and greatest in Po (46.3%),
 205 whereas that of the biochar samples was 8.8–23.7%. Volatile organic compounds are released during
 206 carbonization; therefore, the biochar samples contained less O and H than the raw biomass, resulting in a
 207 lower risk of emissions of certain toxic gases such as carbon monoxide and hydrocarbons [20, 21]. In
 208 addition, the calorific value of fuel increases with decreasing concentration of O in the fuel. Because the N
 209 content in biochars remained stable or increased slightly in DMB, RHB, BGB, and RSB, the N in the

210 investigated biomass was not substantially volatilized under the investigated pyrolysis conditions. The
211 increase in the N proportion of the biomass can be explained by the degradation of amino acids and protein,
212 which are further adsorbed onto the char [22]. The N in the fuels can contribute to the emission of NO_x and
213 other nitrogenous species during the combustion of biomass [23]. However, torrefied biomass (biochar)
214 with increased N does not increase the emission of NO_x, which is instead reduced in most cases [21, 24].
215 Therefore, the expected reduction in volatile matter or gas emission (CO, HCs, NO_x, etc.) and C enrichment
216 in the biochar indicate that fuel quality was improved significantly.

217 3.2. PM emission behavior

218 The PM EFs of all the biomass and biochar samples at different heating temperatures (650, 750, and 850 °C)
219 are presented in Fig. 1. To simply compare PM emissions among the feedstocks, the mean PM EF of each
220 biomass (raw) or biochar (char) sample was calculated by averaging the emission values at three
221 combustion temperatures. The data indicate that PM EF of raw biomass increased in the order: RH < Po <
222 RS < Mi < BG < JL < DM (9.67, 12.93, 13.22, 13.74, 14.58, 15.21, and 19.54 mg/g-fuel, respectively).
223 Meanwhile, the PM EFs of some biomass varied significantly depending on the combustion temperature.
224 For example, for the RS, DM, and Po samples, the EF value increased with increasing combustion
225 temperature, whereas the combustion temperature did not have a significant effect on the PM emissions
226 from RH, BG, Mi, and JL.

227 The average PM EF of biochars increased in the order PoB < MiB < JLB < RHB < BGB < RSB < DMB
228 (1.00, 1.26, 1.30, 1.75, 3.15, 7.84, and 12.99 mg/g-fuel, respectively). Similar to the PM emissions from
229 biomass samples, the PM emissions from some biochars were influenced by the combustion temperature.
230 As the combustion temperature increased, more PM was emitted from RS and DM biochar, whereas the
231 other samples did not show any specific temperature dependency.

232 Pyrolysis significantly reduced PM emission from all the biochar samples, and the magnitude of the
233 reduction varied considerably depending on the combustion temperature of the specific biochar. For
234 example, PM emission was reduced by 75.5% (DM) to 92.66% (Mi) at a combustion temperature of 650 °C,
235 by 14.24% (DM) to 90.74% (Po) at 750 °C, and by 9.64% (DM) to 95.45% (Po) at 850 °C. These results

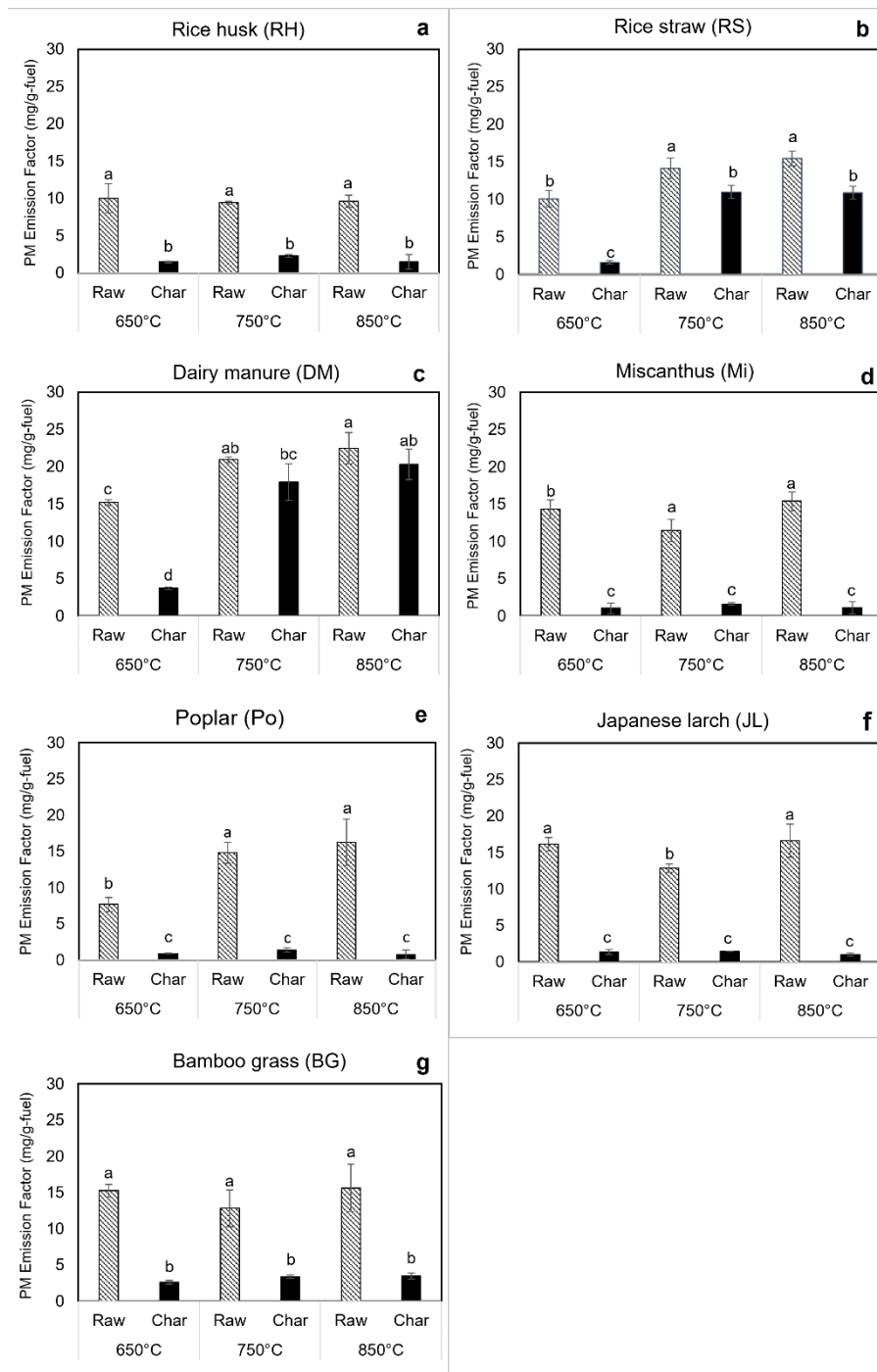
236 indicate that, although the pyrolysis of biomass is effective in reducing PM emission, the efficiency depends
237 on both the feedstock and the combustion temperature [11, 25].

238 The biomass samples containing the greatest amount of VM were Po, JL, and Mi. Consequently, the
239 average PM emission from JL, Po, and Mi was the greatest except for the emission from DM. In the present
240 study, the reduction in VM from biomass due to carbonization ranged from 49.77% to 71.70%, which
241 suggests that VM was efficiently reduced by pyrolysis. The results also indicate that carbonization
242 efficiently reduced PM emissions from low-ash biomass ($\leq 6.7\%$) because of the reduction in VM,
243 irrespective of the combustion temperature (Fig. 1d-g). By contrast, the combustion temperature had a
244 significant effect on the emission of PM from high-ash biochar. For example, DM, which was a biomass
245 with one of the lowest VM contents (71.9%), exhibited the greatest PM emission (19.54 mg/g-fuel), likely
246 because of the emission of PM originating from the ash fraction [11]. Therefore, PM emission from biomass
247 cannot be defined only by VM reduction.

248 The main source of the VM from the lignocellulosic biomass is hemicellulose and cellulose
249 (holocellulose) because they are easily degraded at relatively low temperatures (130-300°C) [5, 18, 26].
250 Whereas the lignin in biomass would degrade more gradually at higher combustion temperatures, the
251 organic and inorganic mineral residue would be collected as bottom ash. The lignin content is highest in
252 woody biomass, whereas herbaceous and other agricultural waste materials are rich in holocellulose and
253 other minerals [5, 18]. Therefore, a higher content of lignin in the parent material might be preferred
254 because it leads to a greater recovery of carbon [5] and produces low PM emissions from biomass fuel [27].

255 As hypothesized, PM emission reduction was most effective at low combustion temperatures (650 °C)
256 for high-ash biochar samples. Higher combustion temperature led to greater PM emissions from high-ash
257 biochars except for RH biochar (Fig. 1a). The PM emissions from RH biochar did not change with
258 combustion temperature. This phenomenon was somewhat counter-intuitive. The average EF of the RH
259 raw sample was 9.67 mg/g, which is similar to that reported by Abah et al. [28]. In their study, the PM EF
260 of rice husk biomass samples was 5.5–13.6 mg/g at combustion temperatures between 600 and 900 °C.
261 However, no comparable study of RH biochar EF has been reported. The surprisingly low PM emission
262 from high-ash RH biochar (Fig. 1a), even at high combustion temperatures, is attributable to compositional

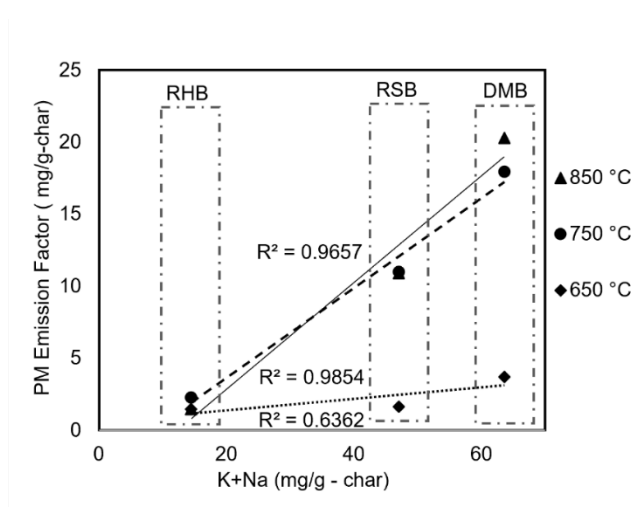
263 differences in the ash. Specifically, RH is known for its high Si content, whereas the other straw materials
 264 are generally rich in K, Ca, and P in addition to Si [29, 30].



265
 266 **Fig. 1** PM emission factor (EF) of raw biomass and biochar (designated as raw and char) samples at
 267 combustion temperatures of 650, 750, and 850 °C [values are mean±standard deviation of three replicates;

268 values with different superscripts within the same biomass group were significantly different, as determined
269 by Tukey's test ($p < 0.05$).

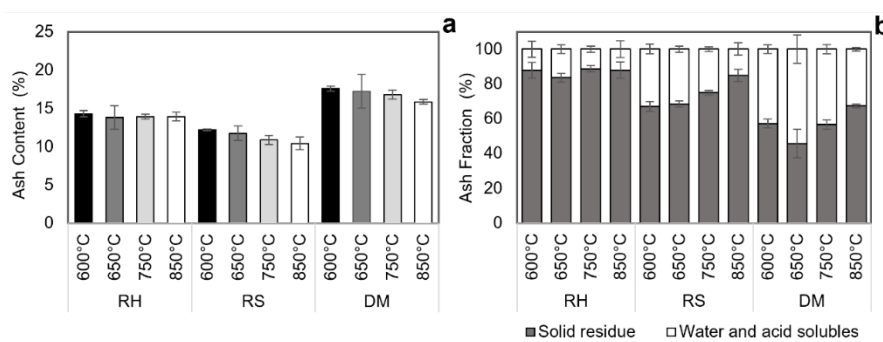
270 Reducing the alkali-metal content in biomass and coal could be beneficial for PM emission reduction
271 [31]. To confirm, this speculation, the K and Na contents of the RH, RS, and DM biochar were compared
272 with their PM EF values at three different temperatures. As shown in Fig. 2, at combustion temperatures of
273 750 and 850 °C, the PM EF of high-ash biochars was strongly correlated with their K+Na content. Higher
274 combustion temperatures significantly promoted the emission of PM because of the greater alkali-metal (K
275 and Na) content. A previous report indicated that the dominant release of alkali metals occurs either below
276 500 °C or above 800 °C [17]. Sublimation of KCl could be the main path of K release [32]. The current
277 study demonstrated that biochar fuel with a high alkali-metal content emitted more PM under high-
278 combustion-temperature conditions. Therefore, the combustion of these biochars at low temperatures could
279 be a reasonable option for PM emission reduction. Further technological studies are required to determine
280 how to reduce the PM emissions and ash content from high-ash-releasing biomass.



281
282 **Fig. 2** Correlation of the alkali-metal content and PM EF for rice husk, rice straw, and dairy manure biochar
283 3.3. Ash composition analysis of high-ash biomass

284 Because of their high ash content and consequently greater PM emissions, the RH RS, and DM samples
285 were subjected to ash heating and fractionation analysis to elucidate the mechanism of PM emission from
286 the ash samples. The mass loss due to heating of the ash samples is depicted in Fig. 3a. When the ash
287 samples (produced at 600 °C) were heated at 650, 750, and 850 °C, the ash weight reduction of the RH ash
288 was 3.25%, 2.62%, and 2.64%, that of the RS ash was 3.63%, 10.95%, and 14.57%, and that of the DM ash

289 was 2.10%, 4.58%, and 9.58% respectively. The insoluble and soluble (in acid) portions of the ash (600 °C)
 290 and heated ash samples (at 650, 750, and 850 °C) are shown in Fig. 3b. The results show that 87.9%, 67.4%,
 291 and 57.2% of the RH, RS, and DM ash samples, respectively, were not digested by the HNO₃ acid system.
 292 A noticeable reduction of the ash weight, representing the soluble part of the ash samples, was observed
 293 when the heating temperature of the RS and DM samples was increased. This result implies that, at high
 294 heating temperatures, soluble (volatile at high temperatures) minerals such as K and Na in the ash can be
 295 emitted as particulate matter, causing a reduction in the ash residue and soluble alkali metals.



296
 297 **Fig. 3** (a) Ash content (%) and (b) solid and insoluble fractions in ash and heated ash of rice husk (RH),
 298 rice straw (RS), and dairy manure (DM).

299 The ash of RS and RH are both dominated by Si (94.7% and 73.2%, respectively); however RS ash has
 300 higher contents of alkali and alkaline-earth metals [33]. The total content of Al, Ca, K, Mg, Na, P, and Fe
 301 in the RH leachates was significantly lower than in the RS and DM leachates (Figs. S1–S3). The dominant
 302 species in the ash sample of RH were K, Fe, and P (5.8, 1.9, and 1.3 mg/g, respectively), whereas the K,
 303 Ca, Fe, and Mg (51.6, 6.1, 3.3, and 1.2 mg/g, respectively) contents in the RS ash were much greater. The
 304 concentrations of other elements were less than 1 mg/g in both the RH and RS ash samples. The DM
 305 contained even greater amounts of Ca, K, P, Na, Mg, Fe, and Al in the ash (100.0, 96.4, 35.5, 17.3, 10.4,
 306 4.2, and 2.3 mg/g, respectively).

307 The water-soluble alkali-metal fraction is likely to be released during combustion, forming PM in the
 308 flue gas, whereas the water-insoluble alkali-metals will likely contribute to ash transformation and ash
 309 melting [29]. Therefore, the acid-soluble (including the water-soluble fraction) alkali content of the three
 310 biomass ash samples was determined and compared with the K and Na contents remaining after the ash
 311 samples were heated at higher temperatures (Table 3).

312 The alkali-metal content was significantly different among the feedstocks. The K content was 5.86,
 313 51.61, and 96.84 mg/g, whereas the Na content was 0.14, 0.52, and 17.33 mg/g for RH, RS, and DM ash,
 314 respectively (600 °C). With an increase in the heating temperature, the alkali-metal content in the RS and
 315 DM ash decreased, whereas that in the RH ash did not. These results imply that the vaporization of alkali-
 316 metals from the ash of DM and RS which might have been released as PM increased with increasing heating
 317 temperature. The same phenomenon was observed in a previous study [11].

318 Table 3. K and Na contents of ash and heated ash samples.

SAMPLE	K (mg/g)			Na (mg/g)		
	RH	RS	DM	RH	RS	DM
Ash	5.86±0.04 ^a	51.61±8.88 ^a	96.84±4.73 ^a	0.14±0.00 ^c	0.52±0.01 ^a	17.33±0.79 ^a
650 °C	5.40±0.08 ^b	61.11±1.51 ^a	94.64±4.32 ^a	0.14±0.01 ^c	0.53±0.01 ^a	18.62±0.88 ^a
750 °C	4.92±0.11 ^c	19.16±1.81 ^b	62.26±3.57 ^b	0.16±0.01 ^b	0.38±0.00 ^b	14.10±0.72 ^b
850 °C	5.89±0.07 ^a	1.29±0.18 ^c	19.36±1.07 ^c	0.25±0.01 ^a	0.15±0.01 ^c	9.52±0.53 ^c

319 RH: rice husk; RS: rice straw; DM: dairy manure. Values in the table represent the mean of three replicates
 320 ± standard deviation. Superscripted letters indicate significant differences within the same column, as
 321 determined by Tukey's test ($p < 0.05$).

322 We attributed the reduction in minerals in the heated ash samples to the vaporization of the alkali metals
 323 because the metal content decreased when the heating temperature was close to the boiling point of the
 324 metals. However, in the RH samples, the alkali (K, Na) content was significantly lower than that in the
 325 other two high-ash biomass types (Table 3). Therefore, the emission of those metals from RH might be
 326 negligible, resulting in lower PM emissions from the RH biochar. Thus, both the ash content and alkali-
 327 metal content appear to strongly influence PM emissions from biochar combustion.

328 4. Conclusions

329 Carbonization significantly reduced PM emissions; however, the efficiency varied depending on the
 330 inherent ash content, the composition of the biomass, and the combustion temperature. When the ash
 331 content was less than 6.7%, the combustion temperature did not significantly influence the PM emission
 332 from either raw or charred samples. In the group of high-ash biomass, the alkali-metal content in the ash
 333 was the main reason for elevated PM emission of biochar samples at higher combustion temperatures.

334 Therefore, the biochar produced from low-ash or low-alkali material can be used as a solid fuel with low
335 PM emissions and enhanced fuel properties. Meanwhile, the biochars with high-ash alkali oxides need to
336 be combusted at a low temperature (650 °C) or the minerals need to be diluted to reduce the risk of emission.
337 Further investigations to reduce the alkali-metal content in ash are needed to enable high-ash biomass to be
338 used as a solid biofuel.

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443 **Author contribution**

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445 Takanori Itoh: Conceptualization, Writing - review & editing, Validation

446 Kazunori Iwabuchi: Conceptualization, Resources, Writing - review & editing, Supervision, Project
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448 Mahmudul Islam Piash: Writing - review & editing

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