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Title	Effects of Ash Composition and Combustion Temperature on Reduced Particulate Matter Emission by Biomass Carbonization.
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Citation	BioEnergy Research, 16, 1629-1638 https://doi.org/10.1007/s12155-022-10526-x
Issue Date	2022-10-22
Doc URL	https://hdl.handle.net/2115/90583
Rights	This is a post-peer-review, pre-copyedit version of an article published in BioEnergy Research. The final authenticated version is available online at: http://dx.doi.org/10.1007/s12155-022-10526-x
Type	journal article
File Information	Effects of ash composition and combustion temperature on reduced particulate matter emission by biomass carbonization.pdf

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Effects of ash composition and combustion temperature on reduced particulate matter emission by biomass carbonization

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Abstract

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

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

Keywords: Biofuel, Pyrolysis, Fuel upgrading, Mineral content

Acknowledgments

The authors acknowledge Associate Professor Dr. Toshihiro Watanabe of the Laboratory of Plant Nutrition at Hokkaido University, Japan for allowing the use of the ICP-MS system and for his valuable advice. We are thankful to Professor Dr. Toshihiko Yamada, Professor Dr. Fuyuki Satoh for their help with the biomass sample collection; and the technical staff at the Field Science Centre of Hokkaido University Mr. Eishi Fujito, and Mr. Yuya Itoh for their assistance with cutting of the bamboo grass from the field. The authors gratefully acknowledge the support of the Mongolia-Japan Higher Engineering Education Development (M-JEED J12B18) project and the DX fellowship grant of Japan.

1. Introduction

Reducing dependency on fossil fuels is important because they are the main source of anthropogenic CO_2 emissions to the atmosphere, have limited future availability, and are nonrenewable. Therefore, biomass-based solid biofuel is gaining popularity worldwide as a sustainable energy source [1]. Biomass fuel is defined as plant- or animal-derived material used as a source of energy to generate electricity or heat. Currently, approximately 3 billion people rely on solid bio-based fuels, such as wood, crop wastes, charcoal, and dung, for their heating and cooking needs [2]. However, the traditional method of utilizing biomass in rural areas is to fuel undeveloped stoves with raw biomass and coal, which has several drawbacks including low energy density and the emission of unhealthy particulate matter (PM) during combustion [3–5]. Consequently, in developing countries, nearly 4 million premature deaths are caused by household air pollution each year, mainly as a result of emissions from biomass combustion [6, 7]. Therefore, to improve the energy density in biofuels and prevent indoor air pollution, technologies for improving biomass-based fuels are critical.

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

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

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

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

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

2. Materials and methods

2.1. Materials

Fourteen samples (raw biomass and their biochar from seven different feedstocks) were used. Feedstocks with different ash contents and resource availability were selected. Rice straw (RS), rice husk (RH), and dairy manure (DM) are wastes generated from agriculture. Giant miscanthus (*Miscanthus giganteus)* (Mi) 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 [wt.%] = 100 – VM [wt.%] – ash [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.] – 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 HNO_3-H_2O_2 system and the liquid

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

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

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

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

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

2.3. PM emission factor measurement

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

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

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

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

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

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

2.4. Statistical analysis

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

3. Results and Discussion

3.1. Fuel properties

3.1.1. Proximate analysis

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

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

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

3.1.2. Ultimate analyses

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

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

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

3.2. PM emission behavior

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

The average PM EF of biochars increased in the order PoB < MiB < JLB< RHB < BGB < RSB < DMB (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 biomass samples, the PM emissions from some biochars were influenced by the combustion temperature. As the combustion temperature increased, more PM was emitted from RS and DM biochar, whereas the other samples did not show any specific temperature dependency.

Pyrolysis significantly reduced PM emission from all the biochar samples, and the magnitude of the reduction varied considerably depending on the combustion temperature of the specific biochar. For example, PM emission was reduced by 75.5% (DM) to 92.66% (Mi) at a combustion temperature of 650 °C, 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 (≤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

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

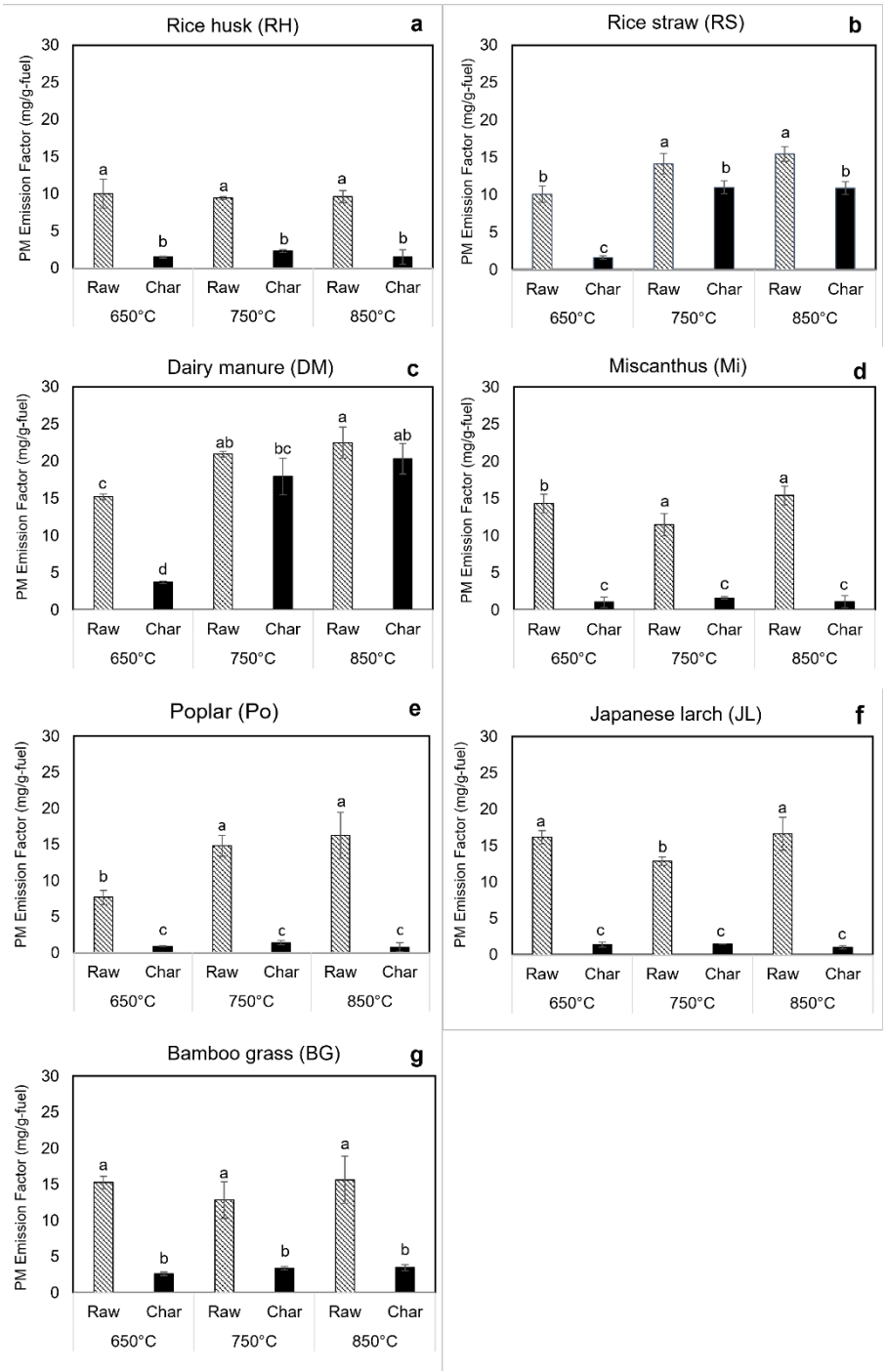


Fig. 1 PM emission factor (EF) of raw biomass and biochar (designated as raw and char) samples at combustion temperatures of 650, 750, and 850 °C [values are mean±standard deviation of three replicates;

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

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

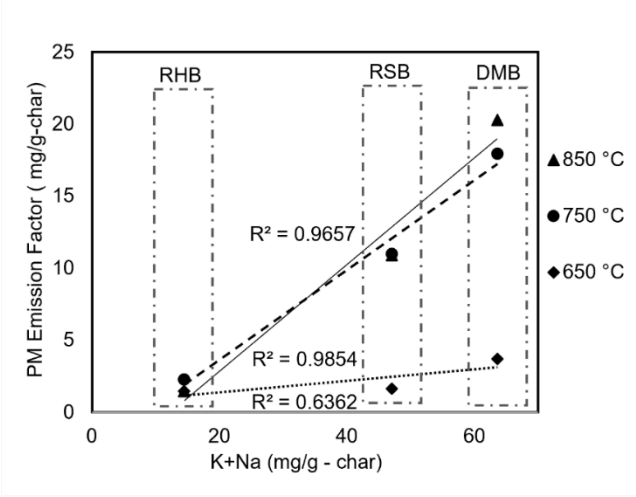


Fig. 2 Correlation of the alkali-metal content and PM EF for rice husk, rice straw, and dairy manure biochar

3.3. Ash composition analysis of high-ash biomass

Because of their high ash content and consequently greater PM emissions, the RH RS, and DM samples were subjected to ash heating and fractionation analysis to elucidate the mechanism of PM emission from the ash samples. The mass loss due to heating of the ash samples is depicted in Fig. 3a. When the ash samples (produced at 600 °C) were heated at 650, 750, and 850 °C, the ash weight reduction of the RH ash 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

was 2.10%, 4.58%, and 9.58% respectively. The insoluble and soluble (in acid) portions of the ash (600 °C) and heated ash samples (at 650, 750, and 850 °C) are shown in Fig. 3b. The results show that 87.9%, 67.4%, and 57.2% of the RH, RS, and DM ash samples, respectively, were not digested by the HNO_3 acid system. A noticeable reduction of the ash weight, representing the soluble part of the ash samples, was observed when the heating temperature of the RS and DM samples was increased. This result implies that, at high heating temperatures, soluble (volatile at high temperatures) minerals such as K and Na in the ash can be emitted as particulate matter, causing a reduction in the ash residue and soluble alkali metals.

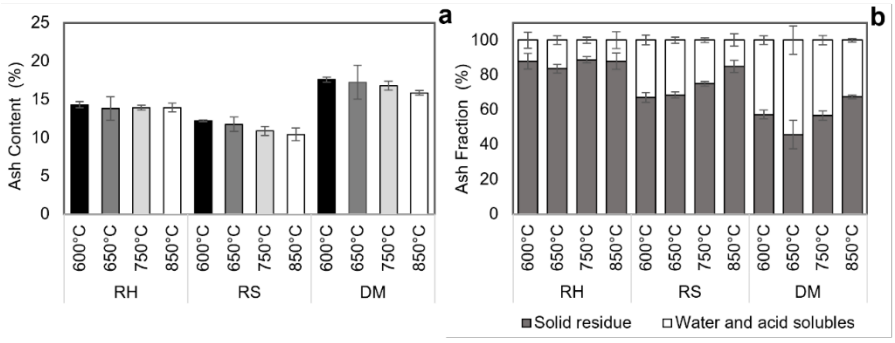


Fig. 3 (a) Ash content (%) and (b) solid and insoluble fractions in ash and heated ash of rice husk (RH), rice straw (RS), and dairy manure (DM).

The ash of RS and RH are both dominated by Si (94.7% and 73.2%, respectively); however RS ash has higher contents of alkali and alkaline-earth metals [33]. The total content of Al, Ca, K, Mg, Na, P, and Fe in the RH leachates was significantly lower than in the RS and DM leachates (Figs. S1–S3). The dominant 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, 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 concentrations of other elements were less than 1 mg/g in both the RH and RS ash samples. The DM 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, 4.2, and 2.3 mg/g, respectively).

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

The alkali-metal content was significantly different among the feedstocks. The K content was 5.86, 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, respectively (600 °C). With an increase in the heating temperature, the alkali-metal content in the RS and DM ash decreased, whereas that in the RH ash did not. These results imply that the vaporization of alkali-metals from the ash of DM and RS which might have been released as PM increased with increasing heating temperature. The same phenomenon was observed in a previous study [11].

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}

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

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

4. Conclusions

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

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

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Statement and Declarations

Funding

The authors gratefully acknowledge the support of the Mongolia-Japan Higher Engineering Education Development (M-JEED J12B18) project and the DX fellowship grant of Japan.

Competing Interest

The authors declare no competing interests.

Ethics declarations: This study did not include human or animal testing. All individuals involved in the experiment were informed about the study's purpose and methods and agreed to participate.

Consent for Publication: All partners agreed to publication in the present form.

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Mahmudul Islam Piash: Writing - review & editing

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