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Effects of pyrolysis temperature and feedstock type on particulate matter emission characteristics during biochar combustion

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ABSTRACT

Aiming to reduce the emission of particulate matter (PM) during biomass combustion, we investigated the effects of pyrolysis temperature and feedstock type on the chemical properties of biochar and PM emission characteristics during subsequent combustion. Wood- and manure-based char samples were prepared at pyrolysis temperatures ranging from 200 to 500 °C and combusted in a laboratory-scale tube furnace at 850 °C. Due to the removal of volatile matter (VM), the total PM emission factor (EF) of the wood char decreased with increasing pyrolysis temperature, becoming negligible with pyrolysis at temperatures over 400 °C. For manure char, although pyrolysis removed VM and reduced the total PM EF from 12.5 ± 2.7 to 5.8 ± 2.9 mg/g-fuel, the high ash content precluded any effect on the emission of ash-derived PM. The occurrence of ash-derived PM resulted from release of Na, Mg, K, and Ca and was enhanced at higher combustion temperatures. We demonstrated that the pyrolysis of low-ash biomass effectively reduces the risk of PM emission. However, the efficacy of thermal treatment of high-ash biomass is limited but might be improved with further treatment, such as ash removal.

1. Introduction

More than 2.6 billion people worldwide use biomass as solid fuel for household cooking and heating [1]. However, burning low-rank fuels in poorly functioning stoves can cause indoor air pollution via the emission of particulate matter (PM), which is associated with serious adverse health effects [2–4]. One approach for reducing PM emissions from household stoves is the use of higher-quality fuels. Ezzati et al. [5] concluded that transitioning from firewood to charcoal would lower the exposure to PM_{10} (PM with an aerodynamic diameter < 10 μm) of most household members and provide more health benefits than would be realized by the use of improved wood stoves. Volatile matter (VM) is a fuel property index often associated with PM emission in coal combustion [6–10]. Chen et al. [11] reported that combustion of low-volatile bituminous or sub-anthracite coal in household stoves is associated with a lower PM emission factor (EF) than combustion of highly or moderately volatile bituminous coal. Li et al. [12] reported that the EF of $PM_{2.5}$ (PM with an aerodynamic diameter < 2.5 μm) increases

with increasing coal VM content to approximately 35% on a dry and ash-free (daf) basis and then remains roughly stable. The results of these studies indicate that combustion of fuels with a low VM content is a useful approach to reduce $PM_{2.5}$ emissions from household stoves. However, the VM content of biomass fuel sources is generally much higher than that of coal [13], suggesting that it is necessary to pretreat biomass to reduce the VM content.

Torrefaction and carbonization are promising processes for enhancing the quality of fuels. In both of these pretreatment processes, biomass is slowly pyrolyzed at temperatures ranging from 200 to 300 °C for torrefaction or > 350 °C for carbonization, accompanied by devolatilization, resulting in conversion of the biomass into biochar [14–17]. The removal of VM during pretreatment produces biochar that is expected to produce lower PM emissions. Indeed, recent studies demonstrated that carbonized biomass emits less PM compared with raw biomass [18,19]. However, producing fuel that produces low PM emission requires careful selection of appropriate pyrolysis conditions. The most important parameter affecting the characteristics of biochar is

pyrolysis temperature; higher temperatures promote devolatilization but increase the ash content of the resulting biochar [20,21]. The ash in biomass is believed to release inorganic PM during combustion [22], and high-ash biomass sources such as agricultural residues produce more PM than woody biomass sources [23]. These observations suggest that the effects of pyrolysis on PM emission characteristics during combustion differ based on feedstock. The wide diversity of biomass sources thus necessitates comprehensive studies to clarify the effects of pyrolysis. Although most previous studies have evaluated emission characteristics using PM EFs determined using gravimetric methods [10,12,18,19], evaluating temporal changes in the PM emission rate (μg-PM min^{-1} g-fuel^{-1}) would provide a greater understanding of PM emission characteristics. In addition to the gravimetric method, such a study could employ the optical sensor developed by Nakayama et al. [24] for real-time monitoring of PM$_{2.5}$ emissions.

The aim of the present study was to elucidate the effects of pyrolysis temperature and type of feedstock on various chemical properties of the resulting biochar and determine the characteristics of PM emission during subsequent combustion. Two different feedstock types (wood shavings and dairy cattle manure) were used as model biomass sources; the former is a commonly used fuel, whereas the latter is a potential fuel in regions with limited forest biomass. We prepared biochar samples with differing VM content by varying the pyrolysis temperature between 200 and 500 °C and compared the PM emission rate and EF of the feedstocks during combustion at 850 °C. In addition, manure ash was heated alone at temperatures ranging from 650 to 850 °C to determine the impact of fuel ash content on the formation of ash-derived PM. Finally, we discuss potential strategies for using high-ash biofuels with minimal PM emission.

2. Materials and methods

2.1. Materials

Wood shavings from *Larix kaempferi* specimens collected in the Tomakomai Experimental Forest of the Field Science Center for the Northern Biosphere, Hokkaido University, Japan, and dairy cattle manure samples obtained from the Experimental Farm of the Field Science Center for the Northern Biosphere, Hokkaido University, Japan, were used as feedstocks in the present study. Prior to biochar preparation, the feedstocks were milled through a 2-mm sieve after drying at 105 °C for 24 h. Wood- and manure-based char samples were prepared in an FO810 muffle furnace (Yamato Scientific, Tokyo, Japan). Feedstock samples were placed in crucibles equipped with lids and pyrolyzed in the furnace at a temperature of 200, 300, 400, or 500 °C for 1 h. The current study also used manure ash derived from dairy manure to investigate the effect of biomass ash on PM emission. The manure ash was prepared by incinerating the manure organic matter in the muffle furnace at 600 °C for 3 h.

2.2. Experimental system

A schematic diagram of the experimental system is depicted in Fig. 1. The system was composed of an air compressor, air receiver tank, mass flow controller (model 8500 series, Kofloc, Kyoto, Japan), quartz glass tube with an internal diameter of 26 mm and length of 500 mm, ARF-30KC tube furnace with an HK01P-11 temperature controller (Heattec, Yokohama, Japan), PM$_{2.5}$ sensor, quartz-fiber filter, and suction pump. For experiments examining the combustion of raw biomass and biochar, approximately 0.5 g of sample was combusted at a temperature of 850 °C and air flow rate of 4.0 L/min, corresponding to 8.0 L/min g-fuel^{-1}, for each trial. For manure ash heating experiments, approximately 0.2 g of sample was heated at a temperature of 650, 750, or 850 °C and air flow rate of 4.0 L/min, corresponding to 20.0 L/min g-ash^{-1}. To assess reproducibility, the sample boat was inserted into the center of the quartz glass tube after the system reached the above-

1: Air compressor; 2: Air receiver tank; 3: Mass flow controller; 4: Electronic tube furnace; 5: Quartz glass tube; 6: Temperature controller; 7: Sample boat; 8: Sensor box; 9: PM$_{2.5}$ sensor; 10: Quartz filter;11: Suction pump
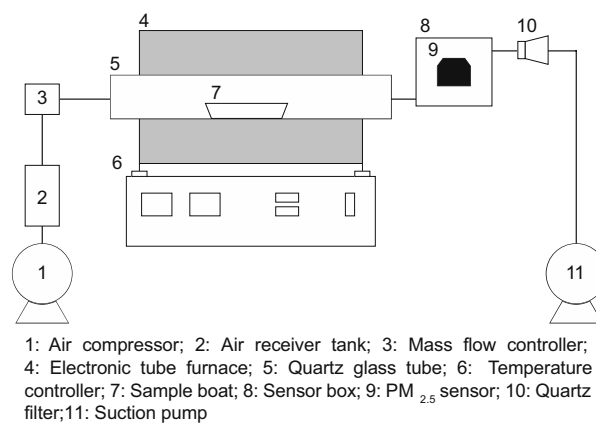
Fig. 1. Schematic illustration of the experimental system.

mentioned conditions. Each trial was conducted at least three times.

The system employed both a PM$_{2.5}$ sensor developed by Nakayama et al. [24] and a model 2500 QAT-UP quartz-fiber filter (Tokyo Dylec, Tokyo, Japan) in accordance with ASTM D2986-95a [25]. The sensor was used to monitor temporal changes in the PM$_{2.5}$ emission rate during combustion, and it was installed in the center of the sensor box to measure the mass concentration of PM$_{2.5}$ at 10-s intervals. The sensor measures the concentration of PM$_{2.5}$ (μg/m^3) based on direct light scattering by particles and estimates particle size based on the intensity of the scattering signals [24]. It should be noted that each trial was commenced only after confirming that the concentration in the sensor box remained stable at 0 μg/m^3 for at least 10 min. The quartz-fiber filter was also used to determine the total PM EF by placing the filter at the outlet of the sensor box and collecting PM using a 4.0 L/min suction pump. Both prior to and after sampling, the filter was reconditioned in a desiccator for 24 h at approximately 25 °C and analyzed gravimetrically. Total PM EF is expressed as mass-based yield (mg/g-fuel).

2.3. Analytical methods

The VM and ash content were determined by heating dried samples at 950 $\pm$ 20 °C for 7 min, in accordance with ASTM E872 [26], and by incinerating the organic matter of the samples at 600 °C for 3 h in the furnace. The amount of fixed carbon (FC) was calculated from the difference (FC = 100 − VM − ash). Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a CE-440 elemental analyzer (Exeter Analytical, North Chelmsford, MA, USA). Oxygen content was calculated by subtraction (O = 100 − C − H − N − ash). For ash analysis, an ICP-MS inductively coupled plasma mass spectrometer (PerkinElmer, Waltham, MA, USA) was used. Ash in biomass and coal generally contains species of alkali and alkaline earth metals [13]; therefore, the current study focused on the contents of Na, Mg, P, K, and Ca. Prior to analysis, manure ash was digested with 60% (w/v) HNO$_3$ at 110 °C in a DigiPREP apparatus (SCP Science, Quebec, Canada) for approximately 2 h.

2.4. Calculations

2.4.1. PM$_{2.5}$ emission rate
The concentration of PM$_{2.5}$ measured using the PM$_{2.5}$ sensor was multiplied by a factor of 1.3 before the calculation, according to a previous study [24]. The PM$_{2.5}$ emission rate at time t can be expressed using the PM$_{2.5}$ concentration at the sensor box inlet:

$$Rate = \frac{f}{W} C_{in},\qquad(1)$$

where *Rate* refers to the emission rate of PM$_{2.5}$ (μg-PM$_{2.5}$ min^{-1} g-fuel^{-1}); f represents the air flow rate (m^3/min); W represents the

sample mass (g); and $C_{in}(t)$ represents the concentration of $PM_{2.5}$ at the sensor box inlet (μg-$PM_{2.5}$/m^3).

To calculate $C_{in}(t)$, we determined the mass of $PM_{2.5}$ in the sensor box at time t as follows:

$$X_t V = X_{t-1} V + (C_{in} - C_{out}) f \Delta t, \tag{2}$$

where X_t and X_{t-1} represent the concentration of $PM_{2.5}$ detected by the sensor at times t and $t-1$ (μg-$PM_{2.5}$/m^3); V represents the volume of the sensor box (m^3); Δt represents the change in time (min); and C_{out} represents the concentration of $PM_{2.5}$ at the sensor box outlet (μg-$PM_{2.5}$/m^3).

Assuming that the $PM_{2.5}$ concentration in the sensor box is uniform, C_{out} can be assumed to be same as the concentration of $PM_{2.5}$ in the senor box, X_{t-1}. Thus, Eq. (2) can be rewritten as follows:

$$C_{in}(t) = \frac{V}{f \Delta t}(X_t - X_{t-1}) + X_{t-1}. \tag{3}$$

2.4.2. VM and PM reduction rates

To evaluate the removal effect of VM on PM reduction, the reduction rates of VM and PM were calculated using Eqs. (4) and (5):

$$Reduction\ rate_{VM}\ [\%] = \left(1 - \frac{VM_{char}}{VM_{feedstock}}\right) \times 100, \tag{4}$$

$$Reduction\ rate_{PM}\ [\%] = \left(1 - \frac{PM\_EF_{char}}{PM\_EF_{feedstock}}\right) \times 100, \tag{5}$$

where VM_{char} and $VM_{feedstock}$ represent the VM content of char and feedstock (%), respectively, and PM_EF_{char} and $PM\_EF_{feedstock}$ represent PM EFs of char and feedstock (%), respectively.

2.5. Statistical analyses

Differences in the content of inorganic elements in manure ash were compared using a one-way analysis of variance. Post hoc Tukey's HSD test ($\alpha = 0.05$) was conducted when significant differences were found. Statistical analyses were carried out using KaleidaGraph, version 4.5.2.

3. Results and discussion

3.1. Chemical properties

The chemical properties of the feedstocks and biochar samples analyzed in this study are summarized in Table 1. Overall, regardless of feedstock type, the VM content decreased with increasing pyrolysis temperature, whereas the FC content increased with increasing

pyrolysis temperature. For example, at a pyrolysis temperature of 500 °C, the VM content decreased from 84.8 to 36.4%db (db: dry basis) for wood shavings and from 69.3 to 16.0%db for dairy manure. The FC content increased from 15.2 to 63.5%db for wood shavings and from 18.3 to 50.6%db for dairy manure at a pyrolysis temperature of 500 °C. These results clearly indicate that pyrolysis removes VM and that the extent of removal increases with increasing pyrolysis temperature.

With regard to ash content, different characteristics were observed between wood shavings and dairy manure. As wood shavings contain very little ash, pyrolysis had no effect on ash content. In contrast, ash accounted for 12.4%db of the raw manure examined in this study and constituted 33.4%db of manure char prepared at 500 °C. This increase in ash content results from the fact that although the ash content does not change during thermochemical processing, the organic material decomposes; therefore, the relative ash content is higher in the resulting char. The same phenomenon has also been reported in previous studies of torrefaction of sewage sludge and livestock manure [27,28].

3.2. PM emission characteristics during wood char combustion

The $PM_{2.5}$ emission rates and total PM EFs during combustion of raw wood shavings and wood char are illustrated in Figs. 2 and 3. For raw wood shavings and wood char pyrolyzed at 200 °C, the emission of $PM_{2.5}$ exhibited a single peak with a long tail that continued for approximately 20 min after the maximum rate was reached. When wood char pyrolyzed at 300 °C was combusted, $PM_{2.5}$ emission exhibited a trend similar to that of feedstock, but there was no tailing of the emission peak. By contrast, the emission rates of wood char samples pyrolyzed at 400 and 500 °C remained constant, at < 0.1 μg-$PM_{2.5}$ min^{-1} g-$fuel^{-1}$, and no clear emission peak was observed during combustion. A consistent trend was also observed with respect to total PM EFs. As pyrolysis temperature increased, the total PM EF for raw wood shavings decreased from 9.3 ± 2.4 mg/g-fuel to 9.0 ± 2.1 mg/g-fuel at 200 °C and to 4.8 ± 0.7 mg/g-fuel at 300 °C and < 0.1 mg/g-fuel at 400 and 500 °C (Fig. 3). The consistent $PM_{2.5}$ emission rates and total PM EFs indicate that a large proportion of the total PM collected on the quartz-filter is $PM_{2.5}$, and this result is in agreement with previous reports indicating that $PM_{2.5}$ accounts for the majority of PM emitted during biomass combustion [10,18].

These results clearly demonstrate that pyrolysis of woody biomass effectively reduces the emission of PM during subsequent combustion. Pyrolysis temperature is associated with PM emissions, and wood char pyrolyzed at temperatures > 400 °C is much less likely to produce PM during combustion. This decrease in PM emissions is due primarily to the removal of VM via the pyrolysis process. As can be seen from Table 1, the VM content of wood char decreased with increasing

Table 1
Proximate and elemental analyses of raw biomass and biochar.

Feedstock	Pyrolysis temperature (°C)	Proximate analysis (%db)			Elemental analysis (%db)			
		VM[a]	FC[b]	Ash	C	H	N	O[c]
Wood shavings	25	84.8	15.2	0.0	48.4	5.8	ND[d]	45.8
	200	84.1	15.8	0.1	50.5	5.8	ND	43.6
	300	53.1	46.9	0.0	64.9	4.3	ND	30.8
	400	49.4	50.5	0.2	76.0	3.0	ND	20.7
	500	36.4	63.5	0.1	79.5	2.4	ND	18.0
Dairy cattle manure	25	69.3	18.3	12.4	43.4	5.4	1.9	36.9
	200	67.9	19.6	12.5	45.4	5.2	1.9	35.0
	300	41.1	36.9	22.0	55.3	3.8	2.6	16.3
	400	27.9	43.5	28.5	53.1	2.6	2.4	13.3
	500	16.0	50.6	33.4	52.2	1.7	2.1	10.7

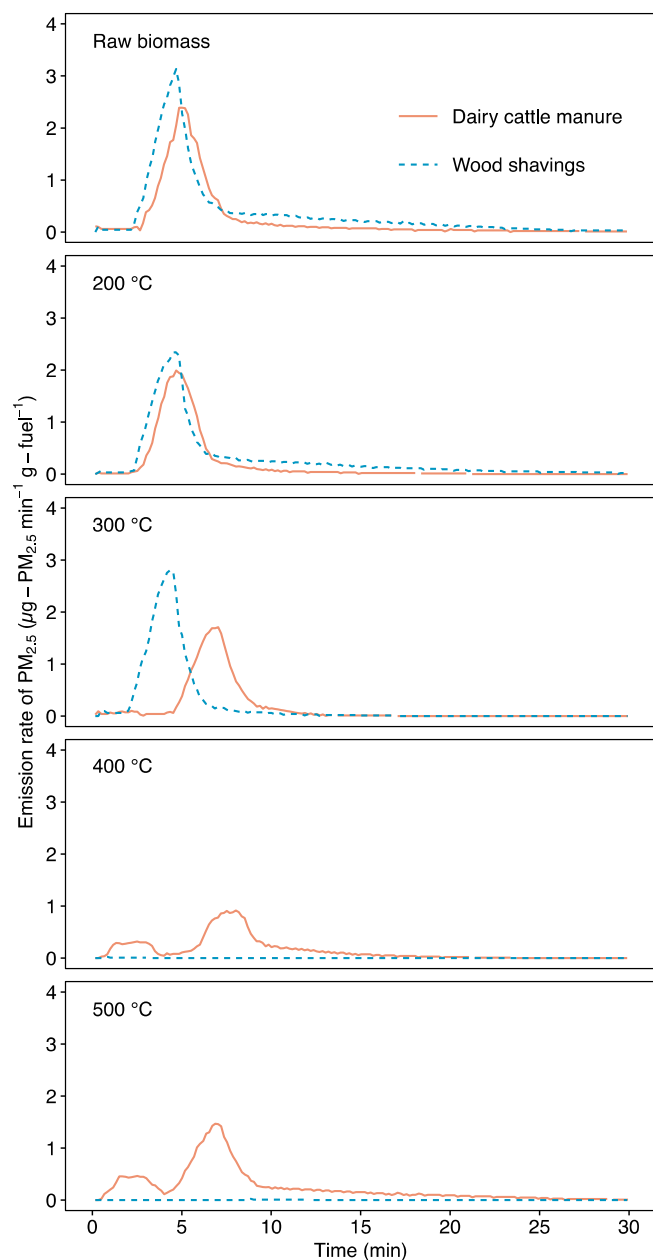[a] Volatile matter.
[b] Fixed carbon.
[c] O = 100 − C − H − N − ash.
[d] Not detected.

Fig. 2. Rates of $PM_{2.5}$ emission from raw biomass and biochar at a combustion temperature of 850 °C. The temperature values indicated in the figure represent the pyrolysis temperature.

Fig. 3. Total PM emission factors for raw biomass (25 °C) and biochar at a combustion temperature of 850 °C.

with a rapid reduction in mass commonly occurs over the temperature range of 200 to 400 °C, whereas the mass reduction is more gradual at temperatures of 400 °C or higher [29–32]. These findings from previous studies are helpful in attempting to explain the characteristics of PM emission from wood char at 300 and 400 °C. The removal of volatile compounds that generate PM still occurs at a pyrolysis temperature of 300 °C and is almost completed when the temperature reaches 400 °C. This difference in the rate of removal of volatile compounds appears to be the likely reason for the different PM emission characteristics for wood char at 300 and 400 °C.

To obtain further insights into PM emissions, we considered differences in biomass composition (e.g., hemicellulose, cellulose, and lignin). Ma et al. [33] reported that the maximum decline in the weight of hemicellulose and cellulose occurs over the temperature ranges of 185 to 325 °C and 290 to 380 °C, respectively, whereas lignin is slowly pyrolyzed at 100 to 800 °C. With respect to biomass composition, these data indicate that hemicellulose and cellulose within a fuel serve as the primary contributors to the production of PM. In other words, pretreatment should entail the removal of hemicellulose and cellulose from the biomass, resulting in a reduction in VM content. Pyrolysis of woody biomass fuels at temperatures > 400 °C would meet this criterion and therefore reduce the risks of indoor air pollution and associated adverse health impacts due to PM emissions.

3.3. Characteristics of PM emission during manure char combustion

The $PM_{2.5}$ emission rates and total PM EFs for the combustion of raw dairy manure and manure char are depicted in Figs. 2 and 3. The $PM_{2.5}$ emission rate of raw dairy manure exhibited a single peak similar to that observed with combustion of raw wood shavings (Fig. 2). During combustion of manure char, the maximum $PM_{2.5}$ emission rate tended to be lower, and the shape of peak broadened. Particularly, combustion of manure char at 400 or 500 °C produced two peaks, clearly indicating that the emission characteristics of $PM_{2.5}$ when manure char is pyrolyzed at temperatures above 400 °C differ compared with pyrolysis at lower temperatures (details discussed below). With regard to the total PM EF, raw manure produced 12.5 ± 2.7 mg/g-fuel of total PM, which was higher than that produced by combustion of raw wood shavings (Fig. 3). Comparing the combustion of raw manure and manure char, the latter exhibited a lower total PM EF, but this value did not become zero as was observed with the combustion of wood char. The total PM EF tended to decrease with increasing pyrolysis temperature, reaching a minimum value of 5.8 ± 2.9 mg/g-fuel when manure char was pyrolyzed at 500 °C.

The combustion of manure char revealed that the effective decrease in PM emissions resulting from pyrolysis of manure is probably due to

pyrolysis temperature. It is recommended to use wood char with a VM content ≤50%db in order to minimize PM emissions. This recommendation is consistent with the results of a previous study demonstrating that lowering the VM content of a fuel reduces the emission of carbonaceous $PM_{2.5}$ [18]. To evaluate the effect of VM removal on the reduction of PM emissions, the relationship between the rates of VM and PM reduction was determined (Fig. S1). The analysis indicated that PM could be reduced by 47.9% when 37.4% of VM was removed, which corresponds to the pyrolysis of wood shavings at 300 °C. Similarly, 99.8 and 100% PM reductions were achieved when 41.7 and 57.1% of VM was removed, respectively (pyrolysis temperatures of 400 and 500 °C). It should be noted that the emission characteristics changed markedly between 300 and 400 °C, although there was no significant change in the VM content of the char samples (53.1%db at 300 °C and 49.4%db at 400 °C; Table 1). Thermogravimetric analyses of various biomass species revealed that thermal degradation of biomass
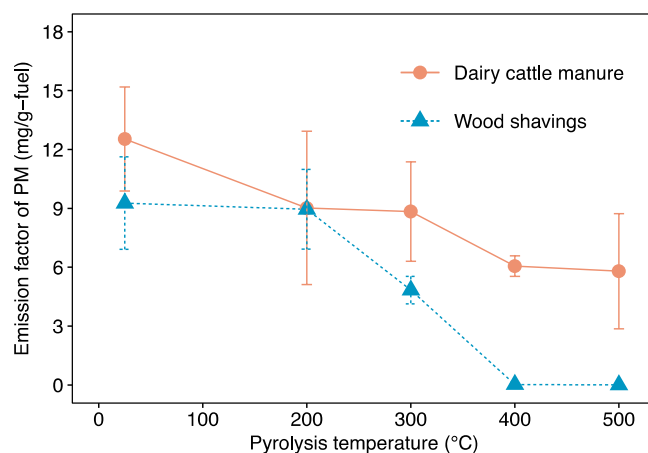
VM removal. However, unlike woody biomass, thermal pretreatment of manure does not sufficiently reduce the likelihood of PM emissions. In fact, pyrolysis of manure at 500 °C removed 76.9% of the VM but reduced the PM by only around 50% compared with raw manure combustion (Fig. S1). On the contrary, pyrolysis at temperatures above 400 °C produces a unique pattern of $PM_{2.5}$ emissions, although this does convert the raw manure into a coal-like material, accompanied by removal of VM (Table 1). The time of the manure char emission peak's appearance at 300 °C was later than that at 200 °C (Fig. 2). One possible reason for this difference is that the ignitability of char might have been lowered due to the decrease in VM content. It is generally known that solid fuels with low VM content, such as coal, exhibit poor ignitability. Thus, it seems natural that the lower the VM content, the longer it would take for the sample to start burning, and the later the emission peak would appear. However, in the case of wood shavings, the time until the appearance of the emission peak was not markedly delayed, despite the lower VM content, indicating that decrease in VM content alone is insufficient to explain the difference. As noted in the Introduction, ash in biomass can affect the emission of PM during combustion [22,23], suggesting that ash in manure char is also associated with PM emissions; therefore, we investigated the impact of ash in manure on PM emission.

3.4. Effect of ash in manure on PM emissions

To confirm whether ash in manure serves as a source of PM emissions from manure-derived fuels, we conducted a heating test of manure ash alone. As the PM emitted from the ash portion was assumed to be associated with the release of inorganic elements, heating tests were carried out at 650, 750, and 850 °C. Figs. 4 and 5 show the $PM_{2.5}$ emission rates and PM EFs during heating of manure ash alone. When heated at 850 °C, the manure ash emitted $PM_{2.5}$, but relatively little $PM_{2.5}$ was emitted with heating at 650 and 750 °C (Fig. 4). The PM EFs agreed well with the $PM_{2.5}$ emission trends, indicating that more PM is released as the heating temperature is increased (Fig. 5).

The results of these heating experiments indicate that ash in manure can serve as a source of PM. Importantly, the emission peak of manure ash heated at 850 °C exhibited peak tailing, which was also observed in the second peak of manure char combusted at 400 and 500 °C (Figs. 2 and 4). These observations suggest that during combustion of manure char of 400 or 500 °C, PM is produced primarily from ash rather than from the organic portion of the char due to the high ash content. Similar results were reported by a previous study. Gao et al. [34] characterized the emission of PM_1 (PM with an aerodynamic diameter < 1 μm) and PM_{10} during combustion of biochar derived from mallee bark at 400 to 550 °C. They reported that higher biochar ash content results in
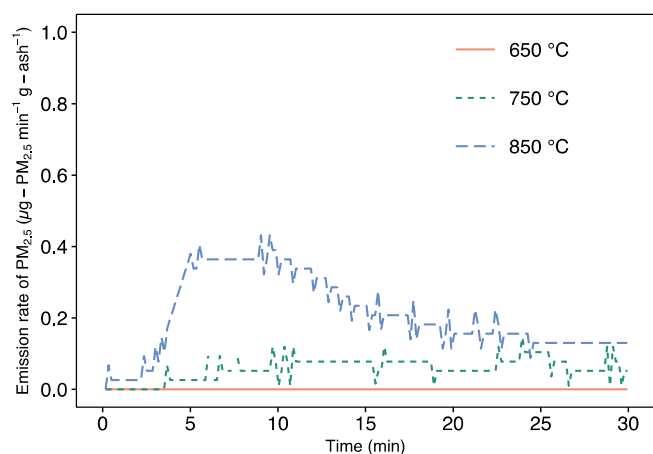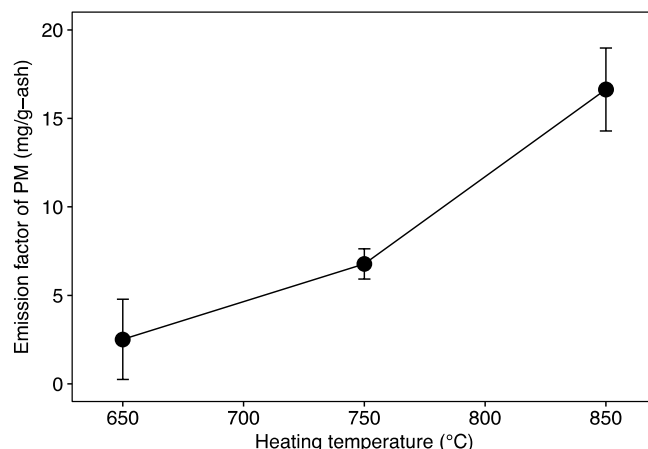

Fig. 5. PM emission factors for manure ash heated at 650, 750, and 850 °C.

significantly higher emissions of PM_1 and PM_{10}. It should also be noted that the two emission peaks of $PM_{2.5}$ resulting from combustion of manure char at 400 and 500 °C observed in the present study—which were not observed in other trials—might have been due to small non-oxygenated reactive species (particularly H free radicals) that are formed upon combustion. These free radicals react with the char to enhance the release of inorganic elements such as Na, K, P, and S, which are involved in the formation of PM_1 during combustion [35]. Although the generation of free radicals would happen with any type of combustion, the impact of these free radicals would be greater during combustion of high-ash fuels. The unique $PM_{2.5}$ emission characteristics of manure char combustion at 400 and 500 °C thus appear to be related to the generation of free radicals. To test this hypothesis, further analyses will be needed relating to the concentrations of elements such as carbon and the metal content in PM on filters collected at the first and second peaks.

We also conducted an ICP-MS analysis of manure ash to characterize the released inorganic elements. Fig. 6 illustrates the changes in the inorganic elemental content of manure ash upon heating. When manure ash was heated at 650 °C, there were no significant changes in Na, Mg, P, K, or Ca content. At heating temperatures of 750 or 850 °C, however, the elemental Na, Mg, K, and Ca (but not P) contents decreased in the order K > Mg > Na > Ca (Fig. 6). A mass-balance analysis of each element revealed the same trend (Fig. S2). The mass loss could correspond to the amount of element that moved into the gas phase due to gas and solid reactions. The analysis revealed that the rate of mass loss increased with increasing temperature; about 77% of K, 70% of Mg,
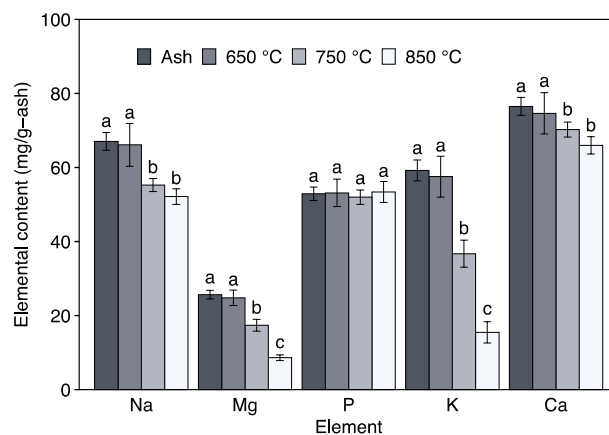

Fig. 4. Rates of $PM_{2.5}$ emission from manure ash heated at 650, 750, and 850 °C.

Fig. 6. Changes in Ca, Na, K, P, and Mg elemental content. Each bar shows the mean ± standard deviation. Different letters represent significant differences as determined using Tukey's test (α = 0.05).
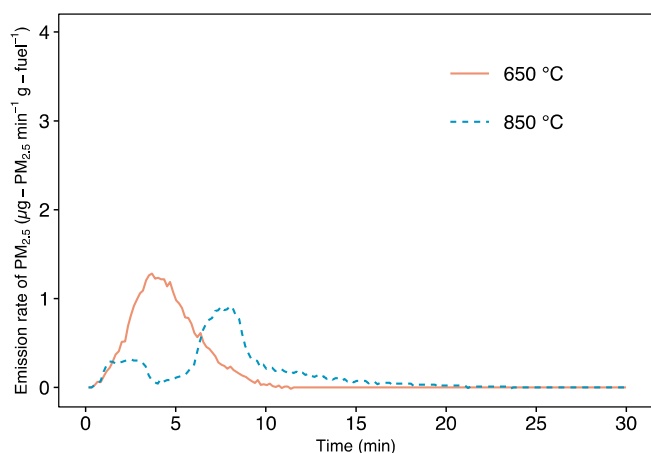
Fig. 7. Rates of PM$_{2.5}$ emission from manure char prepared at 400 °C and combusted at 650 and 850 °C.

30% of Na, and 23% of Ca was released at a heating temperature of 850 °C. The release of Na and K is known to contribute to the formation of PM$_1$, whereas the release of Mg and Ca contributes to the formation of PM$_{1-10}$ [23,36–38], indicating that combustion of manure-derived fuel at temperatures above 750 °C results in the generation of both PM$_1$ and PM$_{1-10}$. Hence, a lower combustion temperature is preferable to suppress the emission of ash-derived PM.

3.5. Potential strategies for mitigating the emission of PM from manure-derived fuels

The results described above confirmed that although combustion of manure char at 400 or 500 °C tends to result in lower PM emissions compared to other feedstocks, emission of PM is not completely suppressed. However, the results of ash heating experiments indicated that the generation of ash-derived PM can be kept to a minimum by heating at relatively low temperatures. Based on this finding, a new hypothesis was developed: setting the combustion temperature lower would further suppress the generation of ash-derived PM. To verify this hypothesis, manure char prepared at 400 °C was combusted at 650 and 850 °C, and the PM$_{2.5}$ emission rate was compared (Fig. 7). Only one emission peak that did not exhibit tailing was produced when manure char was combusted at 650 °C, and PM emission ceased approximately 10 min after the start of combustion. In contrast, combustion at 850 °C produced two emission peaks with tailing. Furthermore, the total PM EF of manure char combusted at 650 °C was 0.9 ± 0.2 mg/g-fuel, which was much lower than that of manure char combusted at 850 °C as shown in Fig. 3. These results suggest that a lower combustion temperature reduces the amount of PM generated in the fuel combustion process by suppressing the generation of ash-derived PM. However, further studies will be needed to verify this hypothesis. In future studies, it will be necessary to ascertain whether reducing the combustion temperature is an effective means of reducing PM emissions for biochar produced under other conditions, as well as to determine the boundary temperature range within which beneficial effects occur.

Apart from altering the combustion temperature to reduce PM emissions, removing ash from biochar may be another worthwhile strategy to consider. With respect to ash removal, water washing is a commonly used, simple treatment process. Cen et al. [39] reported that water washing of corn stalks removes some ash and metallic species while having little impact on physicochemical properties. Lie et al. [40] also reported that pyrolysis combined with subsequent biochar washing removes major ash-forming metals (Na, Mg, K, Ca, etc.) and produces biochar with high fuel quality from different sources of waste biomass. In addition, wet torrefaction (also referred to as hydrothermal carbonization) employing hot compressed water (180–260 °C) may be

another alternative conversion process for enhancing the fuel quality of high-ash biomass sources. Wang et al. [41] reported that wet torrefaction of corn stalks removes 98% more ash compared with dry torrefaction (low-temperature pyrolysis), and Liu and Balasubramanian [42] reported that hydrothermal carbonization of coconut fibers and eucalyptus leaves effectively lowers the contents of Na, Mg, K, and Ca, among others. These studies illustrate a potential strategy for reducing the level of ash-derived PM emissions during biochar combustion. However, potential disadvantages associated with these treatments should also be carefully considered. For example, processing liquids generated by washing or hydrothermal treatments may contain various metals or potentially toxic organic compounds. Thus, comprehensive research considering environmental, energy-related, and economic impacts are encouraged in order to further define the potential uses of high-ash biofuels.

4. Conclusions

Fuel upgrading was performed by thermal pretreatment by focusing on temperature and biomass type to reduce the risk of PM emission during biomass combustion. The combustion test in a tube furnace at 850 °C showed that the total PM EF of the wood char decreased with increasing pyrolysis temperature due to the removal of VM. Although pyrolysis reduced the total PM EF of manure char to some extent, the efficiency was limited due to the release of ash-derived PM. The ash-derived PM resulted from the release of Na, Mg, K, and Ca and was enhanced at higher combustion temperatures. Our results suggested that further treatment could be beneficial, such as ash removal or the use of a low combustion temperature as a means of reducing PM emission from high-ash biomass.

CRediT authorship contribution statement

Takanori Itoh: Methodology, Formal analysis, Writing - original draft, Writing - review & editing.**Nana Fujiwara:**Methodology, Validation, Formal analysis, Investigation, Writing - original draft.**Kazunori Iwabuchi:**Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.**Takumi Narita:**Validation, Investigation.**Dolgormaa Mendbayar:**Validation.**Mitsushi Kamide:**Resources.**Shinobu Niwa:** Resources.**Yutaka Matsumi:**Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2020.106408.

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