HOKKAIDO UNIVERSITY

Title	Methodology for reducing particulate matter emissions during combustion by improving fuel quality of low-grade biomass
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Degree Grantor	北海道大学
Degree Name	博士(農学)
Dissertation Number	甲第15292号
Issue Date	2023-03-23
DOI	https://doi.org/10.14943/doctoral.k15292
Doc URL	https://hdl.handle.net/2115/91542
Type	doctoral thesis
File Information	Dalkhsuren_Davaajav.pdf

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Methodology for reducing particulate matter emissions during combustion by improving fuel quality of low-grade biomass

（低品位バイオマスの燃料品質改善による燃焼時の微粒子状物質排出低減化のための方法論）

Hokkaido University Graduate School of Agriculture

Frontiers in Production Sciences Doctor Course

Dalkhsuren Davaajav

ACKNOWLEDGMENTS

I want to convey my sincere gratitude to everyone who has supported me throughout my years-long Ph.D. journey; without their help, my thesis would not have been completed as it is.

I would like to begin by sincerely thanking my supervisor, Prof. Iwabuchi Kazunori, for the opportunity to study in Japan and conduct this research. I can't thank him enough for all of his hard work, constant guidance, and encouragement, which enabled me to finish this thesis. I absolutely admire his vast expertise, patience, and trust in me to carry on this very new research area to me.

Furthermore, I would like to give special thanks to my dissertation committee, Prof. Shigenobu Koseki, and Asso. Prof. Naoto Shimizu for their invaluable time and insightful feedback which greatly aided me in improving my thesis.

I want to thank every one of my lab mates at the Agricultural Biosystem Engineering Laboratory for their willing help with any matter I ask of them, as well as for every research discussion and every lab dinner party. I owe a debt of gratitude to Dr. Takinori Itoh and Dr. Mahmudul Islam Piash since writing this thesis would not have been feasible without their essential guidance, revision, constructive criticism, and general support throughout my studies. I also would like to thank Mr. Takumi Narita and Mr. Hinata Tateno for their help with my experiments.

I want to 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. I would like to thank Prof. Toshihiko Yamada and Prof. Fuyuki Satoh for their help with the biomass sample collection and the technical staff at the Field Science Centre of Hokkaido University, as well as Mr. Eishi Fujito and Mr. Yuya Itoh for their assistance with cutting of the bamboo grass from the field. I would like to thank all the technical staff and managers of the Global Facility Center for their assistance in measuring the composition of my samples.

My heartfelt thanks go to the members of the research project group as well as the financial support granted by the MJEED, Mongolia Japan Higher Engineering Education

Development project, which allowed me to conduct this research and study in Japan. I would especially want to thank Prof. Nachin Baatarbileg and Asso. Prof. Sukhbaatar Gerelbaatar, my mentor and the team leader of our research team at the National University of Mongolia. Since my bachelor's degree, their continued support, understanding, and guidance have enabled me to pursue my academic career.

Last but not least, I'd want to thank my family, which includes my brothers and sisters, my father Khalzan Dalkhsuren, and my mother Dorjgotov Jamiyansuren. With their unwavering love and psychological support, any hardship felt passable. Furthermore, my chosen family - my friends - have greatly aided me in navigating this Ph.D. journey, particularly Ms. Bayarsaikhan Tsevelmaa and Dr. Nergui Enkhzaya as well as Dr. Jargalsaikhan Battsetseg, for sharing their experiences and simply discussing the same challenges we face. I would like to say a big thank you to all the friends I made in Sapporo; without their help, care and the days we spent together, living alone in a foreign country would have been difficult.

Dalkhsuren Davaajav

Jan. 2023

EXECUTIVE SUMMARY

The ever-increasing energy demand will lead to more exploitation of fossil fuels and subsequent emission of greenhouse gases into the atmosphere. Instead, carbon-neutral biomasses can be utilized as alternate solid fuels. Although it has the potential to substitute fossil fuels, low energy density and particulate matter (PM) like pollutants' emission during combustion makes it an unpopular alternative. Given that PM emission is one of the leading causes of 4 million premature deaths by household air pollution each year, it is an urgent issue that must be addressed. Hence, increasing energy density and reducing PM emissions is essential to utilize biomasses as a renewable fuel source and to alleviate health issues caused by household air pollution.

Thermochemical pre-treatments, including carbonization, have been suggested as an effective method to valorize biomass. One of the key features of carbonization is the enrichment of fixed carbon (FC), and reduction of volatile matter (VM) of biomass fuel by producing energy-dense biochar. The produced biochar is expected to reduce PM emissions during combustion due to the reduction of VM. However, the benefits of carbonization, particularly PM reduction, might not be equal for all types of biomasses because of composition heterogeneity and differences in combustion conditions. Therefore, an assessment of PM emission reduction by carbonization of various types of biomasses at different combustion temperatures is required. In this study, seven different types of biomasses (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. As a result of carbonization, recovery of carbon was greater than 50% for all biomasses except dairy manure, and PM emissions were reduced by as much as 95.5%. It implies the potential of carbonization for biomass fuel quality improvement. PM reduction was significant 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. Therefore, to limit PM emissions from the chars produced by high ash biomass, a lower combustion temperature is preferable.

A considerable amount of PM can be emitted during the combustion of biochars that are produced from low-grade biomass (LGB), even after a significant amount of VM was reduced by the carbonization process. We hypothesize that mineral transformation occurs in high-ash biochar during the combustion at higher temperatures and that releases as PM. Therefore, in this study, the emission factor of high ash-containing biochar was investigated at combustion temperatures between 650 to 850 °C. The PM emission from these biochar samples was increased with the increase in combustion temperature. The composition of minerals in the ashes of rice straw, rice husk, and dairy manure was investigated before and after heating at different temperatures (650, 750, and 850 °C). Mineral analysis revealed that enhanced PM emission from ash-rich biochar samples can be attributed to a greater concentration of Na and K and the melting of their compounds at higher combustion temperatures. We also found that co-combustion of low-ash biochar with high alkali-containing biochar may effectively reduce the PM emission, mainly by the mineral dilution mechanism. Considering the suggested approaches to reducing PM emissions, further research is required to develop field utilization of biochar as a solid fuel product

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CHAPTER – 1. GENERAL INTRODUCTION

1.1. Background to the study

Energy is a fundamental and indispensable need for humans to survive and develop. Therefore, with population growth, energy demand and consumption have soared. Because of their low cost and abundance in early industrialization, fossil fuels were introduced in the last century, exacerbating the environmental crisis. Currently, the combustion of fossil fuels accounts for 85% of global energy demand. It is estimated that the energy demand of the world will increase by 1% per year by the year 2040 (Agency 2022). However, considering the emissions of greenhouse gases (including CO_2), and the non-renewability of fossil fuel, the substitution of it for clean and renewable energy is a major challenge in the energy sector. The developed countries of Europe and the US have started to shift primary energy consumption to net carbon-zero sources including nuclear, wind, solar, hydro, tidal, and biomass. Meanwhile, a large part of the world still relies on the combustion of local biomass including wood, animal feces, and other agricultural and forestry residue for cooking and localized heating.

Biomass usage as a solid fuel is expected and encouraged globally due to its numerous benefits, which include its renewable nature, carbon neutrality, and reduction of harmful pollutant emissions such as sulfuric and nitrous oxides. Despite the recognized importance of biomass for the shift from fossil fuel to renewable energy, the combustion of raw biomass causes serious health problems in people due to indoor air pollution caused by particulate matter (PM) emissions. Considering the widespread availability and associated benefits of biomass use, lowering PM emissions during combustion will save lives and alleviate health issues caused by indoor air pollution while being a sustainable alternative to fossil fuel.

1.2. Literature review

1.2.1. Biomass

Biomass is a naturally occurring organic material that is directly or indirectly driven by living species including all plants and animals (Basu 2013; Van Loo and Koppejan 2008). The main sources of biomass are agricultural (food grain, all types of stalks, seed hull, nutshells, and manure), forest (trees, wood waste, bark, sawdust timber slash), municipal (sewage sludge, refuse-derived fuel, food waste, wastepaper, and yard clipping), energy crops (poplar, willow, switchgrass, alfalfa, prairie bluestem, corn, and soybean) and biological origin (animal waste, aquatic species, and biological waste). The European committee for standardization has divided the biomasses into two major groups – virgin (primary) biomass, and waste biomass (secondary). The virgin biomass includes woody plants and leaves (lignocellulosic), grasses, energy crops, cultivated crops, and aquatic biomass. Whereas the waste biomass is solid and liquid wastes generated from agriculture and municipal solid waste, sewage, animal and human wastes, and methane gas derived from landfill (Basu 2013). It is estimated that 140 billion metric tons of biomass are produced annually from agriculture all over the world (Ok et al. 2019). Due to its wide availability and renewable nature, biomass-based solid biofuel is gaining popularity worldwide as a sustainable energy source (Erni et al. 2020).

Due to its origin, and type the composition is considerably different but the principal types of biomasses are cellulosic (non-cereal), starch, and sugar (non-cereal). The majority of the biomass is lignocellulosic means the main constituent is cellulose, hemicellulose, and lignin polymers which generally cover 20–40, 40–60, and 10–25 wt.% respectively (McKendry 2002; H. Yang et al. 2007). Photosynthesis and plant respiration result in the production of a diverse and chemically complex array of structural and non-structural carbohydrates and other compounds including the 3 main polymers, lipids, proteins, simple sugars, starches, HCs, and ash which along with water comprise a majority of the biomass. Each class compound's concentration varies depending on resource, species, type of plant tissue, stage of growth, and growing conditions.

The degradation and transformation rate of the main polymers influences the thermo-kinetic properties, combustion efficiency, and pollutant emission rate of biomass.

Hemicellulose is the most reactive of the 3 main components of biomass and decomposes at a temperature of about 220-315 °C, whereas cellulose decomposes at temperatures between 280 and 400 °C (H. Yang et al. 2007; Burhenne et al. 2013). Compared with the two, lignin is a complex three-dimensional macromolecule, its degradation occurs in a broad range of temperatures starting at 200 °C due to the various functional groups with different thermal stability (H. Yang et al. 2007; Weber and Quicker 2018). Thus, the composition of biomass is an important factor for various thermal properties when used as solid fuel.

Biomass contains a large number of organic compounds (Carbon – C; Hydrogen – H; Oxygen – O; N – Nitrogen; may also have small amounts of chlorine and sulfur), moisture, and a small number of inorganic impurities known as ash. The degradation of the biomass structure during conversion results in the reaction of various components and, in some cases, their undesirable emission. The concentration of various species, as well as the conversion method and parameters, all have an impact on the release of pollutants. Therefore, the usage of various biomass materials derives several issues due to their composition differences and uncertainties of thermochemical transformation.

Solid fuel constituent is generally evaluated by proximate analysis which gives the composition of the biomass in terms of gross components of moisture, fixed carbon (FC), volatile matter (VM), and ash (Fig. 1-1). The VM of fuel is the amount of condensable or non-condensable vapor that is released when the fuel is heated. Biomass has a high content of volatile matter due to its high content of water, oxygen, and other extractives (Basu 2013).

The heating value (calorific value) of the biomass is highly correlated with the C, and O content ratio. Therefore, the ultimate analysis of biomass is used to evaluate biomass efficiency as solid fuel. Once the biomass is burned, the inorganic plant nutrient compounds form ash and remain as residue and most of the other elements are emitted.

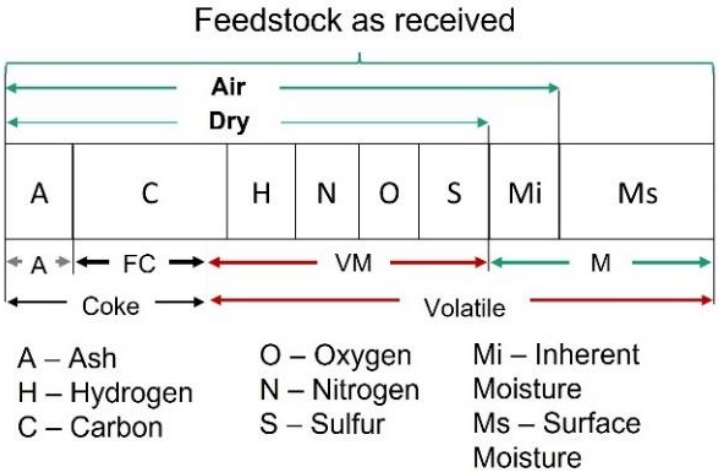


Fig. 1-1 Basis of expressing fuel composition

1.2.2. Combustion of biomass

Energy production from biomass generally, can be achieved by thermochemical conversion including, direct combustion, pyrolysis, carbonization/torrefaction, gasification, and liquefaction. The combustion of biomass is the oldest and most widely used thermochemical technique of all thermochemical conversions to produce heat and electricity. The nature of the combustion process depends on both the combustion environment and fuel properties. The phases of the combustion are drying, devolatilization (pyrolysis), flaming combustion, and char combustion.

Drying is the first step in the solid fuel-burning process, where moisture begins to evaporate at temperatures below 100 degrees Celsius. Since evaporation consumes the energy released during the combustion process, the moisture content of the fuel must be kept to a minimum to ensure stable combustion. Devolatilization is the phase in which pyrolysis reaction (except the process occurs in completely inert conditions) occurs when a biomass fuel thermally decomposes and releases

- light permanent gases (such as H_2, CO, CO_2, CH_4, H_2O, NH_3),
- tar (condensable hydrocarbon),
- char (the remaining devolatilized solid waste residue) and
- inorganic compounds (K, P, N, S, and Cl) elude from the solid particle (Williams et al. 2012).

As a result of devolatilization char and volatiles are produced (Williams et al. 2012). During devolatilization, many of the bonds and linkages in cellulose and hemicellulose (C-O bond); lignin (O functional groups, and C in aromatic rings) break and rearrange forming carbon-rich gas molecules. Simultaneous with the gas molecules escaping through pores during the phase, more stable fragments rearrange to form new stronger interactions with neighboring structures, and these stronger interactions accumulate to form char particles (Basu 2013).

Flaming combustion is defined as the rapid oxidation of volatile species after they have been released from the fuel particle. Due to the volatile oxidize release rate during combustion, there is a significant amount of overlap between devolatilization and flaming combustion (Meca 1999). Like other steps of combustion, the char burning step of biomass also can co-exist with the devolatilization step. It is reported that 10-30 % of the biomass represents formed chars. Char or charcoal can be produced by a separate process but it is one step of biomass combustion (Williams et al. 2012).

These sub-processes will occur concurrently within the fuel bed in a real-world application with continuous fuel feeding. In households, for cooking and heating biomass has generally combusted in various low-temperature traditional simple stoves (600-900°C), and three-stone fires (Gill-Wiehl, Price, and Kammen 2021; Raman et al. 2013; Illerup et al. 2020). Several studies have tested improved stove adoption to reduce public health risks. There was no substantial reduction in PM emission when 17 commonly used simple stoves in Asia and Africa were compared to improved stoves (Garland et al. 2017). A comprehensive review study has revealed that stove users are still reluctant to transition to improved stoves due to the ease of use, cooking pattern, and cost-effectiveness of the old stoves (Gill-Wiehl, Price, and Kammen 2021).

1.2.3. Particulate matter

As defined by the United State Environmental Protection Agency, particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets (Morakinyo et al. 2016). The size of PM varies and is expressed by mass concentration $PM_{0.1}$ (aerodynamic diameter less than 0.1 μm), $PM_{2.5}$, (aerodynamic diameter less than 2.5 μm), or PM_{10} (aerodynamic diameter less than 10 μm). Depending on the size of the PM, the potential

to cause health issues is varied. Both respirable (ultrafine – $PM_{0.1}$ to fine particles $PM_{2.5}$) to inhalable (coarse particles – PM_{10}) particles, cause diverse health issues (Morakinyo et al. 2016). Short-term and long-term exposure to PM induces daily mortality and chronic effect on human health, respectively (Tarín-Carrasco et al. 2021; WHO 2021). It is estimated that in Europe, the excess mortality rate from $PM_{2.5}$ is 904,000 premature deaths per year. This mortality rate tends to rise by 73% in the year 2050 (Tarín-Carrasco et al. 2021). World Health Organization (WHO) remarked that PM affects more people than any other pollutants (WHO 2021). Thus, when the concentration of the particles is reduced, associated mortality will decrease by 20-50% (Bruce et al. 2015). Therefore, it is apparent that each source of PM emission must be investigated, and appropriate mitigation measures applied. Household air pollution contributes significantly to outdoor air pollution, about 80 percent of PM is emitted from household fuel firing (for cooking and heating) in both urban and rural areas (Jaworek et al. 2021), accounting for up to 50% in some parts of the world. Air quality measurements are commonly reported in terms of daily or annual mean PM_{10} particle concentrations per cubic meter of air volume (m^3). Typical air quality measurements express such PM concentrations in micrograms per cubic meter (μg /m^3). Fine particle concentrations ($PM_{2.5}$ or smaller) are also reported when sufficiently sensitive measurement tools are available.

In 2021, the WHO set the following targets and guidelines for household air pollution concentrations: PM_{10} 15 μg/m^3 annual mean, 45 μg/m^3 24-hour mean; $PM_{2.5}$ 5 μg/m^3 annual mean, 15 μg/m^3 24-hour mean. However, the WHO reported in 2019 that 90% of the world's population is living in conditions where the guideline levels are not met (WHO 2021). For instance, in Ulaanbaatar, the capital city of Mongolia the emission factor of $PM_{2.5}$ 24-hour mean in the urban area and the suburban area was 52.8 μg/m^3 and 127.8 μg/m^3 respectively (Enkhbat et al. 2016). The high PM concentration in a suburban area was due to raw coal and biomass burning in the households (Lim et al. 2018). The WHO target and recommendations are intended to assist in meeting the guideline for pollution in all settings, both indoors and outdoors. However, due to the difference in housing characteristics and cooking practices (Fig. 1-2), the emission of pollutants in a household differs significantly.

Fig. 1-2 Example of traditional stoves in Mongolia and Nepal

According to WHO, household target emission rates from combustion need to be $PM_{2.5}$ 0.80 mg/min and 0.23 mg/min for vented and unvented combustion respectively. The emission evaluation has to consider the emission factor, kitchen volume, air exchange rate, and daily cooking time (World Health Organization 2021). Thus, to ensure a healthy environment and effectively reduce the PM, the factors of PM emission during the combustion of the most widely used fuel materials in households of every nation need to be evaluated precisely.

PM formation and emission during combustion

Throughout the combustion process, the inorganic mineral components and organically bound metal compounds in solid fuels gradually release volatile alkali metal salts, chloride salts, sulfate salts, or heavy metal salts, among other things, while forming ash via a series of physical and chemical processes (Niu, Tan, and Hui 2016). The main phase of the release of PM during combustion is devolatilization and the formation of PM due to the high heating of char is impacted by the swelling, permeability, and volatile evolution rates of solid fuel particles, as well as the transformation of inorganic matter including the generated ash particles (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). Depending on the particle size distribution formation of the ultrafine, fine, and coarse particle is different.

Under the different combustion phases, the nucleation and condensation process will greatly govern the emission of ultrafine and fine particles. The coarse particles are made up of unburned carbon and high melting point compounds that are generally internal and

externally bound minerals in the fuel matrix. As a result of internal mineral melt polymerization and external mineral and unburnt carbon fragmentation coarse PM is produced (Y. Wang et al. 2017; Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020) The major pathways of fine particles are the precipitation of inherently fine inorganic minerals and its fragmentation aggregation of ultrafine particles rich in volatile alkali metal salts, and uneven condensation of evaporative substances on fine residual ash particles. Additionally, the combustion temperature has a significant impact on the emission of ultrafine and fine-mode PM. (Jia and Lighty 2012).

Fuel composition effect on PM emission

To understand and predict the performance of solid fuel, the chemical composition is fundamental. Therefore, the influencing factors need to be discussed comprehensively. The composition and pollutant emissions of coal have been studied well since it has been the most common fuel for small-scale combustion and large-scale utilization.

As previously mentioned, due to biomass composition differences in moisture, FC, VM, and ash content, the emission of PM is varied during the combustion. Previous studies have reported the effect of VM content in fuel matrix as the main pathway of emissions from biomass and coal (Li et al. 2016; Chen et al. 2018). During coal combustion, incomplete combustion is the main reason for various pollutant emissions including black carbon of elemental carbon. Whereas in biomass combustion, the main emission of PM is due to the early degradation of the hydrocarbons into lighter volatiles (Li et al. 2016).

Recent studies have demonstrated the ash content of biomass is playing a significant role in the emission of PM from biomass combustion (Wei Yang et al. 2017; Itoh et al. 2020). Inorganic constituents include dissolved salts, organically bound ash-forming compounds, and included and excluded minerals all influence the emission behavior of PM (Kleinhans et al. 2018). The ash melts when the combustion temperature is above the boiling point, and some minerals in the ash are liberated, which is a primary source of PM emissions.

Phase transformation of the ash is the main reason for the PM release from the ash, when the melting has occurred some minerals in the ash are released when the combustion

temperature exceeds their boiling points. Considering the PM emission induced by ash mineral is regulated by the combustion temperature largely (Míguez et al. 2021; Kleinhans et al. 2018). Therefore, the evaluation of the PM emission from the fuel needs to be tested in various temperature ranges which should be in line with the field measurements of small-scale household stoves. Organic and inorganic components in the ash are associated with the solid and fluid phases' transformation during the combustion of biomass. Solid phases include crystalline and nanocrystalline to semi-crystalline minerals. Whereas the fluid matters are mostly inorganic, including the gas and gas-liquid association (Vassilev et al. 2017). As reviewed by Wu Yang et al., the fuel material composition and combustion environment all influence the emission of PM during the combustion (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020).

1.2.4. Particulate matter-reducing technologies

To reduce the emissions of PM during the combustion in households in developing countries the stove-improving method has been tested, for instance, the government of Mongolia implemented the improved stove project with the support of the Asian development bank during the last decade (ADB 2019). The results of PM emission reduction however have shown no significant results compared with using the old stove (Lim et al. 2018). Therefore, the upgrading of biomass fuel is necessary. To upgrading of the fuel, several pre-treatment methods have been suggested including physical methods of drying, briquets, and some thermochemical and thermophysical methods including water and acid washing to remove alkalis, or torrefaction to reduce VM (Sun et al. 2019; Jensen, Sander, and Dam-Johansen 2001; van Lith et al. 2006; Itoh et al. 2020).

Among the pre-treatment methods, thermochemical pre-treatment of biomass, which includes torrefaction and carbonization is considered the most efficient and simple technology. Torrefaction and carbonization are both based on pyrolysis reaction which partially decomposes biomass and that results in the creation of biochar via fuel composition change. Pyrolysis has previously been observed to be an effective technique to both increase energy density and reduce PM emission during combustion due to the removal of VM (Li et al. 2016; Itoh et al. 2020). Pyrolysis is the same as the initial stage of combustion and gasification but the difference is the pyrolysis process requires an absence of oxidizing substances or when the supply is restricted. During the pyrolysis of

biomass, complex hydrocarbon molecules will be decomposed into smaller and simpler molecules of gas-liquid and char which is more energy-dense than the parent feedstock (Basu 2013).

Carbonization is a process of making biochar by slow pyrolysis, in the temperature range of 500 to 900 °C (Yogalakshmi K N et al. 2022). Itoh et al. investigated various pyrolysis temperatures to minimize PM emissions from biomass and found that carbonization may efficiently reduce PM while reserving carbon content at pyrolysis temperatures over 400°C (Itoh et al. 2020). Further, the study suggested that the reduction of PM emissions might not only be related to the reduction of the VM, also its efficiency was significantly different depending on the composition of the parent material.

1.3. Research problem identification

There are 2.8 billion people who still rely on coal and traditional biomass as primary energy for cooking and heating. Therefore, minimizing the fossil fuel and exploitation of valuable forest biomass resources, Low-Grade Biomass (LGB) including energy coppice, agriculture, or forestry waste materials utilization is advantageous. As reviewed from the literature, direct combustion of those materials is not encouraged due to the emission of PM and its risk to human health and environmental pollution. On the other hand, compared with coal combustion, biomass combustion has less toxic emissions (SO_2 NO_x) due to the low content of sulfur or nitrogen (Zhang et al. 2007). Given the potential for waste reduction, LGB fuel would be beneficial if the fuel qualities, such as energy density and PM emission during burning, were adequately addressed.

To improve biomass quality, thermochemical pretreatment processes are beneficial, particularly carbonization, which increases carbon content while decreasing hydrogen and oxygen content as a result of volatile matter (VM) emission. However, one of the unwanted components is ash content, which frequently increases. The release of organic VM and certain inorganic minerals (ash) from the fuel matrix is the primary source of PM emissions during carbonized biomass burning (Shen et al. 2021; Long et al. 2012). It has been claimed that the high ash content of biomass may reduce the effectiveness of carbonization in reducing PM (Itoh et al. 2020). It indicates that the efficacy of carbonization on PM reduction is debatable for some biomass with greater ash content.

Therefore, evaluating the efficiency of PM reduction by carbonization based only on the reduction of VM is might not valid. The capacity of carbonized biomass as clean fuel requires a comprehensive and accurate evaluation for future efforts of PM emission control.

The combustion temperature is one of the defining factors for the emission of a PM that originates from the ash part of fuel during combustion. However, studies of PM emissions from biomass or coal ash content and composition have focused on applications in industrial combustion systems. Thus, PM emission measurements have generally been above 1200 °C (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020) which is a relatively higher temperature than the stove bed temperature used in households. Depending on the combustion temperature, and the main elements in the ash composition, various ash transformations could occur. Alkali metals, for example, are reactive species that function as a catalyzer during combustion, increasing the ignition temperature, lowering the melting temperature of ash, or vaporizing easily depending on the behavior of other ash elements. However, the influence of the ash mineral component of biochar on PM emission during combustion has received insufficient attention.

Thus, the impact of the biochar ash mineral transformation on PM emission needs to be studied considering the uneven stove temperature. Additionally, to promote the affordable clean utilization of waste-derived biochar material as solid fuel, precise calculation of the different biochar's emission factors (EF) and influencing factors on emission behavior must be investigated. These results of EF and PM emission behavior of biochar during various ranges of combustion temperature might make it possible to design household PM emission mitigation methodology.

1.4. Aims and objectives

In the present work, to clarify the PM emissions from various types of biomasses and their carbonized products, and to propose a potential method for reducing PM emissions based on ash content and composition, we hypothesized:

1. Low combustion temperatures reduce the PM emissions from carbonized biomass, even biomass with high ash content.

2. Mineral transformation occurs in high-ash biochar during the combustion at higher temperatures and that is released as PM.

1.5. Thesis outline

Chapter – 1 will provide an overview of the current situation of renewable energy concerns. As biomass is a renewable carbon-neutral source of energy, biomass combustion needs to be supported. However, its pollutant emission issue needs to be addressed since ambient air pollution causes severe diseases in humans. Therefore, this chapter will review the literature and rationalize the research need related to biosolid fuel.

Chapter – 2 The chapter will provide experimental data on the PM emission factor from biomass combustion and reduced PM emission due to carbonization.

Hypothesis: Low combustion temperatures reduce the PM emissions from carbonized biomass, even from biomasses with high ash content.

Objective: To investigate the PM emission from various biomasses and their carbonized product, to study the effect of feedstock composition and combustion temperature on the reduction efficiency of PM emission.

Chapter – 3 This chapter will focus on reducing the PM emission from the high ash-containing biochar (RHB, RSB, DMB).

Objectives: To investigate PM EF in various combustion temperatures, mineral content analysis of the high ash-containing biomass and reveal the mechanism of PM emission originating from ash.

Hypothesis: Reducing the K content in the high-ash biochar will suppress the PM emission during combustion at less than 850°C.

Chapter – 4 is for an overall discussion of the thesis, further implications and study suggestions will be provided.

CHAPTER - 2. EFFECTS OF ASH CONTENT AND COMBUSTION TEMPERATURE ON REDUCED PARTICULATE MATTER EMISSION BY BIOMASS CARBONIZATION

2.1. Abstract

Thermochemical pre-treatments, including carbonization, have been suggested as an effective method to valorize biomass. One of the key features of carbonization is the enrichment of fixed carbon (FC), and reduction of volatile matter (VM) of biomass fuel by producing energy-dense biochar. The produced biochar is expected to reduce PM emissions during combustion due to the reduction of VM. However, the benefits of carbonization, particularly PM reduction, might not be equal for all types of biomasses because of composition heterogeneity and differences in combustion conditions. Therefore, an assessment of PM emission reduction by carbonization of various types of biomasses at different combustion temperatures is required. In this study, seven different types of biomasses (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. As a result of carbonization, recovery of carbon was greater than 50% for all biomasses except dairy manure, and PM emissions were reduced by as much as 95.5%. It implies the potential of carbonization for biomass fuel quality improvement. PM reduction was significant 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. Therefore, to limit PM emissions from the chars produced by high ash biomass, a lower combustion temperature is preferable.

2.2. Introduction

To utilize LGB as effective biofuel through carbonization, we need to thoroughly investigate their PM emission behavior and its probable sources. To address the problems associated with solid biofuel, several pretreatment strategies, including physical, chemical, thermophysical, thermochemical, and biological methods, have been examined (Sun et al. 2019; Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). 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 (Li et al. 2016; Itoh et al. 2020). 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 (Itoh et al. 2020). They also reported that the 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 (Itoh et al. 2020).

Like dairy manure, numerous types of waste-derived biomass have a high ash content and are usually considered low-grade biomass (LGB) (Vassilev et al. 2010). PM emissions due to the enhanced ash content of the carbonized biomass are 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 (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). 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 (Vassilev et al. 2010). 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 (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). 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 (Illerup et al. 2020). 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.

2.3. Materials and methods

2.3.1. Materials

Fourteen samples (raw biomass and their biochar from seven different feedstocks) were used as shown in Table 2-1. 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.)* (Po) is a representative fast-growing forest coppice, and Japanese larch (*Larix kaempferi)* (JL) is an abundant tree species of temperate forests. Bamboo grass (BG) from *Sasa kurilensis* is an invasive species in the temperate forest of northern Japan. All raw biomass samples were collected from the experimental farm and campus of Hokkaido University, Sapporo, Japan. The samples were dried at 105 °C for 24 h to remove inherent moisture, then milled and sieved through a 0.5-mm sieve.

Table 2-1. Feedstock information

Feedstocks Type	Feedstock forms abbreviation	
	Raw	Carbonized
Rice Husk	RH	RHB
Rice Straw	RS	RSB
Dairy Manure	DM	DMB
Miscanthus (Miscanthus Gagenthus)	Mi	MiB
Poplar (Populus spp)	P	PoB
Japanese Larch (*Larix kaempferi*)	JL	JLB
Bamboo grass (*Sasa kurilensis*)	BG	BGB

Biochar samples were produced by pyrolysis of the biomass at 400 ℃ for 1 h in a FO810 muffle furnace (Yamato Scientific, Tokyo, Japan). Biochar samples were designated as RSB (rice straw biochar). A pyrolysis temperature of 400 °C was selected on the basis of the high char yield and efficiency of VM reduction at this temperature (Itoh et al. 2020). To determine minerals that could contribute to PM emissions, ash was heated at different temperatures (650, 750, and 850 ℃) using some high-ash (>10%) biomass *(*e.g., RH, RS, and DM). The ash samples were prepared by incineration of the raw materials in a muffle furnace at 600 ℃ for 3 h and were subsequently stored under airtight conditions. After the samples were incinerated, 300 mg of each ash sample was heated at 650, 750, or 850 ℃ for 60 min in a tube furnace. The products are referred to as heated ash samples.

2.3.2. Fuel compositional analysis

Proximate analyses including VM, FC, ash content, and ultimate analysis (carbon, hydrogen, and nitrogen contents) of the biomass and biochar samples were evaluated. The VM content of raw and carbonized biomass was determined according to the method specified in standard ASTM (i.e., heating the dried feedstock at 950 ± 20 °C for 7 min). For determination of the ash content, samples were combusted at 600 °C for 3 h in a muffle furnace. The fixed carbon (FC) content was calculated by the difference (FC [wt.%] = 100 – VM [wt.%] – ash [wt.%]).

The carbon, hydrogen, and nitrogen contents of the samples were determined using a CE-440 elemental analyzer (Exeter Analytical, North Chelmsford, MA, USA). The

oxygen content was calculated by subtraction (O [%db.] = 100 – C [%db.] – H [%db.] – N [%db.] – ash [%db.]).

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.

To determine the chemical composition of the samples, ash of RH, RS, and DM was analyzed by scanning electron microscope (SEM) coupled with Energy Dispersive Spectrometer (EDS) (JEOL JSM-7001FA, USA). The instrument was operated at an accelerated voltage of 10 kV, 20 kV

2.3.3. PM emission factor measurement

To compare the emissions of total suspended PM during the combustion of 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. (Itoh et al. 2020), except that we did not use a PM emission sensor. The furnace design and experimental design are illustrated in Fig. 2-1. 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 the 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.

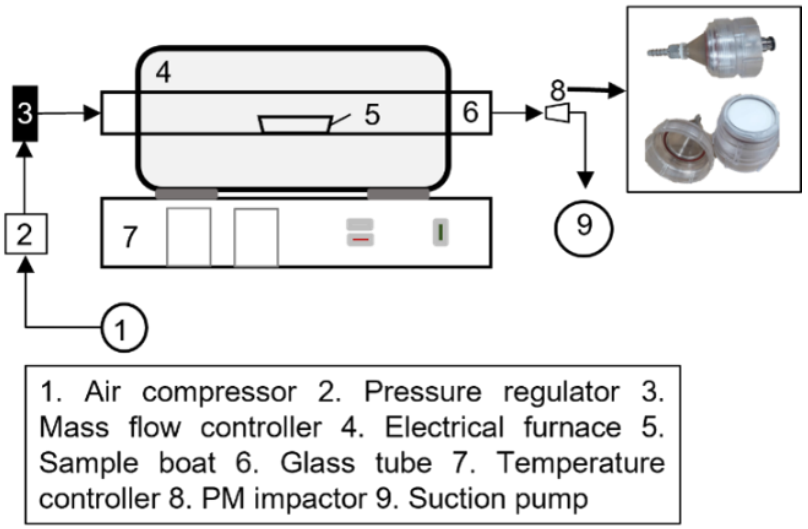


Fig. 2-1 Furnace design and experimental setup

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 were 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. (Itoh et al. 2020).

To compare the efficiency of carbonization 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.

2.3.4. Statistical analysis

To determine the difference among the treatments shown in Fig. 2-3, 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. 2-3) analysis within the same raw and carbonized material of each

feedstock. A correlation test between the PM emission factor and the K and Na content in the biochar samples was conducted in MS Excel.

2.4. Results and Discussion

2.4.1. Fuel compositional study

2.4.1.1. Proximate analysis

The results of the proximate and ultimate analyses of all feedstock and biochar samples are summarized in Table 2-2. 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 of animal and human-derived biomass > herbaceous and agricultural biomass > woody biomass (Vassilev et al. 2017). The ash content based on the 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 increased in the order JLB < PoB < MiB < BGB < RSB < RHB < DMB. Because of pyrolysis, the ash content of the biochars produced from high-ash raw materials (RH, RS, DM) increased significantly, whereas the ash content in the other samples increased only slightly.

Table 2-2. 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

Overall, the increase in FC and ash content in biochar samples was due to VM release as a result of carbonization. The VM reduction rate (Table 2-3) due to carbonization was greatest in BG (71.70%) followed by RH, RS, Mi, DM, Po, and JL. Itoh et al. reported that woody biomass that contains less than 50% VM can be used to minimize PM emissions (Itoh et al. 2020), suggesting that the risk of PM emission due to VM would be sufficiently reduced by the method proposed in the present study.

Table 2-3 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

2.4.1.2. 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 ratio of the H/C and O/C of raw and biochar samples are illustrated using the Van Krevelen diagram (Fig. 2-2). The overall reduction of the atomic ratio suggests an increase in fuel quality similar range of coal. 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 2-3). All materials underwent C enrichment due to dehydration and decarboxylation during the carbonization 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 (Weber and Quicker 2018; Chen et al. 2018). Similar to the observation of Weber and Quicker (Weber and Quicker 2018), 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 (Basu 2013; Burhenne et al. 2013).

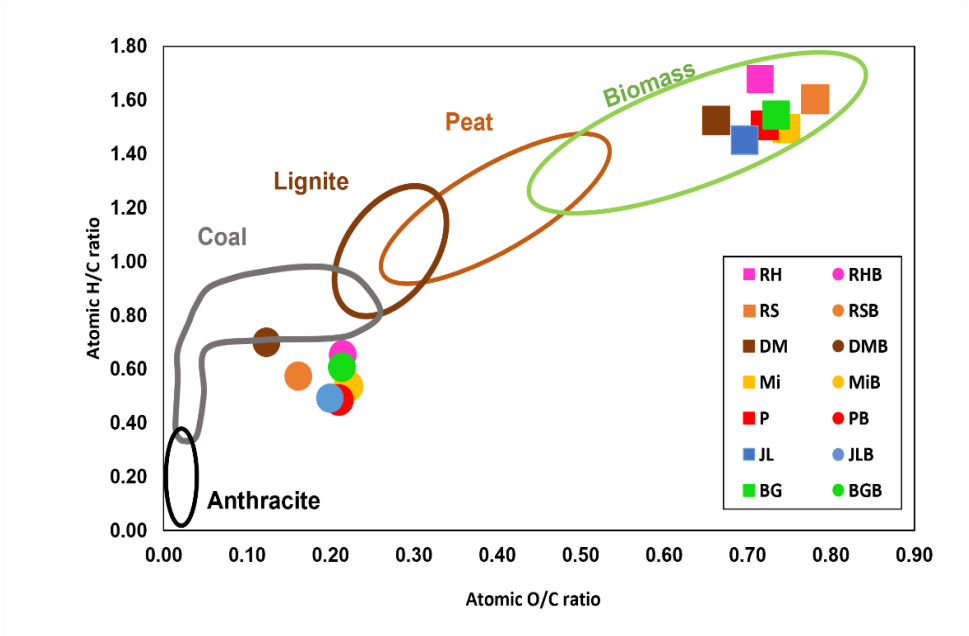
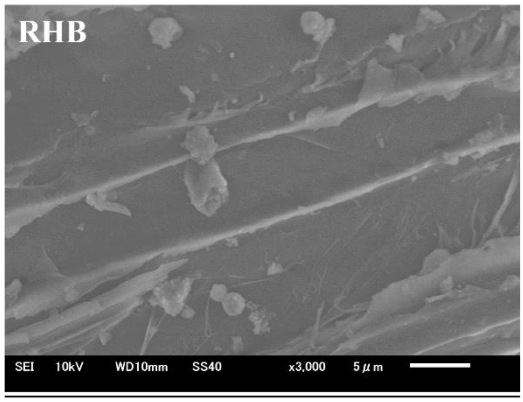


Fig. 2-2 Van Krevelen diagram of raw biomass and biochar

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 (Fitzpatrick et al. 2007; Maxwell et al. 2020). 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 (Riaza et al. 2019). The N in the fuels can contribute to the emission of NO_x and other nitrogenous species during the combustion of biomass (Broer and Brown 2015). However, torrefied biomass (biochar) with increased N does not increase the emission of NO_x, which is instead reduced in most cases (Maxwell et al. 2020; Nunes 2020). 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.

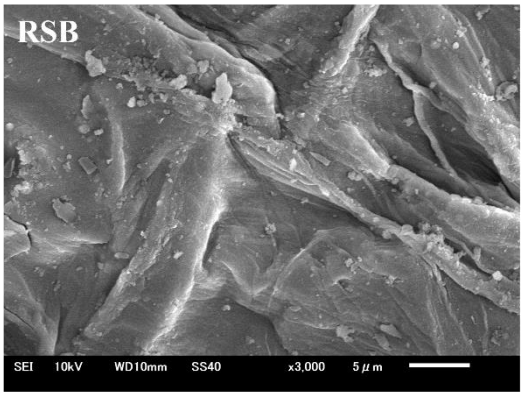
2.4.1.3. Biochar surface analysis

In solid fuel surfaces, the elemental composition is an important factor to evaluate the reactivity and emission of PM during combustion. Therefore, to analyze the mineral composition of the produced biochar the surface mineral component of each biochar material has been presented in Fig. 2-3 to Fig. 2-9. The K, Na, S, and Cl are considered highly volatile species during thermal treatment; therefore, they will easily vaporize during the gaseous phase. Whereas, Si, Al, Ca, Fe, Mg, P and are considered non-volatile and tends to retain in biomass char during the devolatilization stage (Valmari et al. 1998)



Element	Content (%)	Element	Content (%)
C	56.9	Fe	0.0
O	26.6	Mg	0.1
Si	15.3	Ca	0.1
K	0.6	P	0.0
Al	0.1	S	0.0
Na	0.0	Cl	0.0

Fig. 2-3 SEM-EDS image of RHB



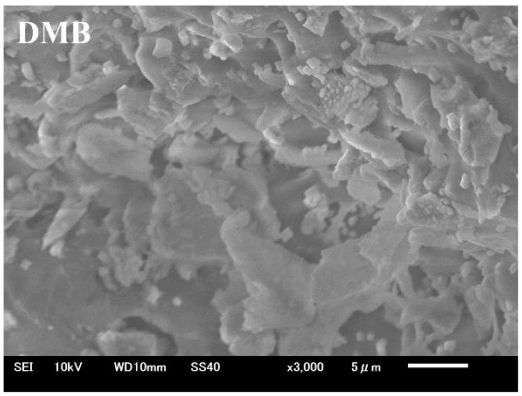
Element	Content (%)	Element	Content (%)
C	59.5	Fe	0.4
O	29.5	Mg	0.1
Si	2.3	Ca	0.3
K	3.8	P	0.0
Al	0.8	S	0.0
Na	0.4	Cl	0.0

Fig. 2-4 SEM-EDS image of RSB

The volatile alkaline species (K, Na) content is highest in DMB, 3.1%, and lowest in JLB, 0.0%, (DMB > RSB > BGB > PoB > RHB > MiB > JLB). The S content was not detected on the surface of all biochar, whereas some trace amount of Cl has been observed on the DMB (1.7%) and BGB (0.1%). K and Na, S, and Cl often dominate the fine particulate matter of fly ashes (Valmari et al. 1998). Therefore, the high content of those volatile elements in biochar is expected to contribute to more fine PM emissions (Kortelainen et al. 2015). Si, Al, Ca, Fe, Mg, and P the non-volatile elements, could cause the emission of coarse PM during char combustion by partitioning from the fuel matrix (Kortelainen et al. 2015). As shown in Fig. 2-3 RHB is significantly rich (15.3%) in Si compared with all other biochars. The second high Si-containing biochar is RSB (Fig. 2-

4). It is known that the annual plant tissue, shell, or hull is rich in Si which is an essential element for mechanical function, for instance, it strengthens the plant cell and the protection from fungal and pest attacks.

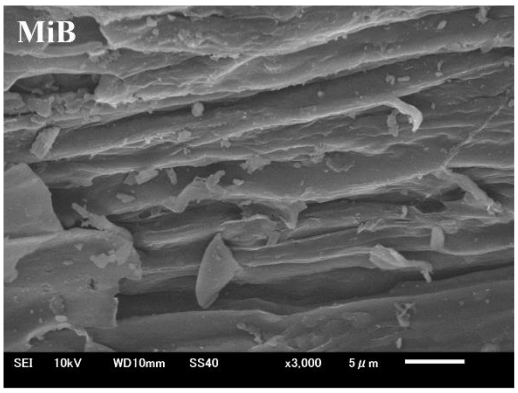
The component of DMB was highly heterogeneous along with high content of alkaline minerals and other alkaline earth metals (Ca and Mg) observed. The ash content of RSB and DMB and the amount of reactive elements is the highest, therefore it is expected to emit higher PM emissions.



Element	Content (%)	Element	Content (%)
C	64.5	Fe	0.2
O	27.2	Mg	0.6
Si	1.4	Ca	0.8
K	2.1	P	0.2
Al	0.3	S	0.0
Na	1.0	Cl	1.7

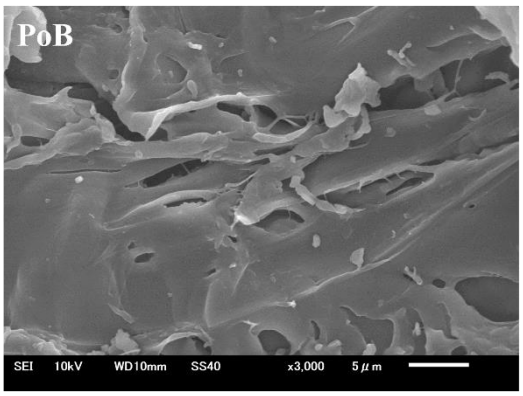
Fig. 2-5 SEM-EDS image of DMB

The low ash-containing biochar contained a significantly high amount of C (73.1 - 75.0%) when compared with the high ash biochar (56.9 - 64.5%). The same phenomenon has been observed by the proximate analysis. Due to the less heterogeneous component of the low ash containing biochar lower emission of PM is expected. The surface morphology of the woody biochar (PoB, JLB) has been observed significantly different than the other biochars (Fig.2-7, Fig.2-8). The porous structure of the biochar material is might due to the retainment of the highly complex and hardy vascular system of woody plants (Słupianek, Dolzblasz, and Sokołowska 2021). Considering the limitation of SEM analysis which only could detect and estimate the composition of minerals on the surface of the materials, furthermore accurate quantitative mineral composition analysis is required.



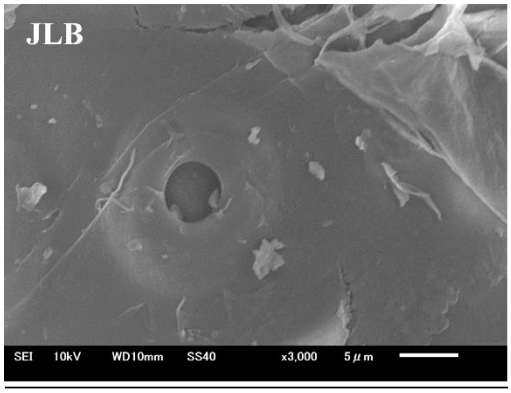
Element	Content (%)	Element	Content (%)
C	75.0	Fe	0.1
O	23.6	Mg	0.1
Si	0.2	Ca	0.6
K	0.1	P	0.0
Al	0.3	S	0.0
Na	0.1	Cl	0.0

Fig. 2-6 SEM-EDS image of MiB



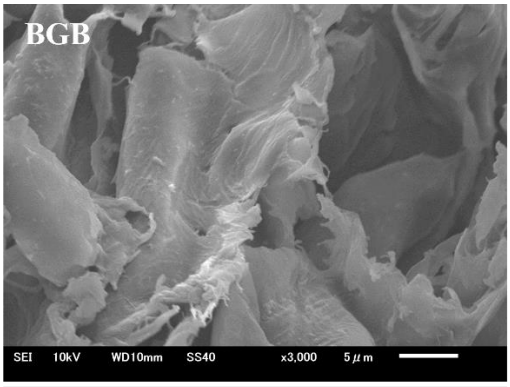
Element	Content (%)	Element	Content (%)
C	74.2	Fe	0.0
O	23.7	Mg	0.3
Si	0.0	Ca	0.5
K	0.7	P	0.0
Al	0.1	S	0.0
Na	0.1	Cl	0.0

Fig. 2-7 SEM-EDS image of PoB



Element	Content (%)	Element	Content (%)
C	74.6	Fe	0.1
O	24.9	Mg	0.0
Si	0.0	Ca	0.2
K	0.0	P	0.0
Al	0.2	S	0.0
Na	0.0	Cl	0.0

Fig. 2-8 SEM-EDS image of JLB



Element	Content (%)	Element	Content (%)
C	73.1	Fe	0.0
O	24.3	Mg	0.1
Si	0.3	Ca	0.0
K	1.1	P	0.0
Al	0.3	S	0.0
Na	0.1	Cl	0.1

Fig. 2-9 SEM-EDS image of BGB

2.4.2. PM emission reduction

The PM EFs of all the biomass and biochar samples at different heating temperatures (650, 750, and 850 °C) are presented in Fig. 2-10. 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 (9.7, 12.9, 13.2, 13.7, 14.6, 15.2, and 19.5 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 (1.0, 1.3, 1.3, 1.7, 3.1, 7.8, and 12.9 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.

Carbonization 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 92.6% (Mi) at a combustion temperature of 650 °C, by 14.2% (DM) to 90.7% (Po) at 750 °C, and by 9.6% (DM) to 95.4% (Po) at 850 °C. These results indicate that, although the carbonization of biomass is effective in reducing PM emission, the efficiency depends on both the feedstock and the combustion temperature (Itoh et al. 2020; Li et al. 2019).

The biomass samples containing the greatest amount of VM were Po, JL, and Mi. Consequently, the average PM emission from JL, Po, and Mi was the greatest except for the emission from DM. In the present study, the reduction in VM from biomass due to carbonization ranged from 49.7% to 71.70%, which suggests that VM was efficiently reduced by carbonization. The results also indicate that carbonization efficiently reduced

PM emissions from low-ash biomass (≤6.7%) because of the reduction in VM, irrespective of the combustion temperature (Fig. 2-10d-g). By contrast, the combustion temperature had a significant effect on the emission of PM from high-ash biochar. For example, DM, which was biomass with one of the lowest VM contents (71.9%), exhibited the greatest PM emission (19.5 mg/g-fuel), likely because of the emission of PM originating from the ash fraction (Itoh et al. 2020). Therefore, PM emission from biomass cannot be defined only by VM reduction.

The main source of the VM from the lignocellulosic biomass is hemicellulose and cellulose (holocellulose) because they are easily degraded at relatively low temperatures (130-300 °C) (Basu 2013; Chen et al. 2018; Ma et al. 2015). Whereas the lignin in biomass would degrade more gradually at higher combustion temperatures, the organic and inorganic mineral residue would be collected as bottom ash. The lignin content is highest in woody biomass, whereas herbaceous and other agricultural waste materials are rich in holocellulose and other minerals (Basu 2013; Chen et al. 2018). Therefore, a higher content of lignin in the parent material might be preferred because it leads to a greater recovery of carbon (Basu 2013) and produces low PM emissions from biomass fuel (Lv et al. 2010).

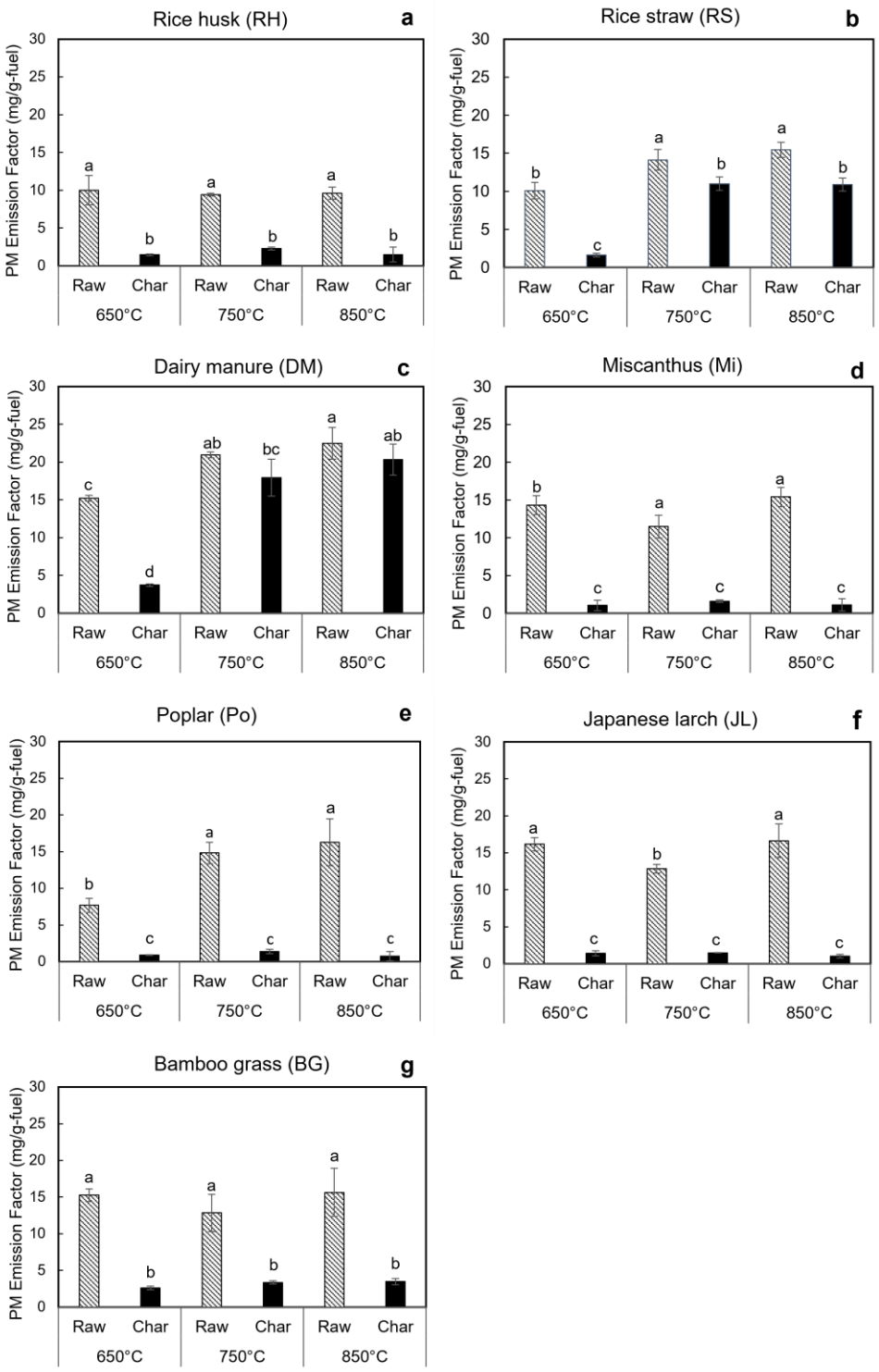


Fig. 2-10 PM emission factor (EF) of raw biomass and biochar (designated as raw and char) at combustion temperatures of 650, 750, and 850 °C [values are mean±standard deviation of three replicates; values with different superscripts within the same biomass group were significantly different, as determined by Tukey's test (p<0.05)].

As hypothesized, PM emission reduction was most effective at low combustion temperatures (650 °C) for high-ash biochar samples. Higher combustion temperature led to greater PM emissions from high-ash biochar except for RH biochar (Fig. 2-10a). The PM emissions from RH biochar did not change with combustion temperature. This phenomenon was somewhat counter-intuitive. The average EF of the RH raw sample was 9.67 mg/g, which is similar to that reported by Abah et al. (Abah, Ahamed, and Noguchi 2020). In their study, the PM EF of rice husk biomass samples was 5.5–13.6 mg/g at combustion temperatures between 600 and 900 °C. However, no comparable study of RH biochar EF has been reported. The surprisingly low PM emission from high-ash RH biochar (Fig. 2-10a), 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 (Beidaghy Dizaji et al. 2022; Wei Yang et al. 2017).

2.5. Conclusion

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 might be 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.

CHAPTER - 3. REDUCTION OF PM EMISSION FROM HIGH-ASH BIOCHAR

3.1.Abstract

A considerable amount of PM can be emitted during the combustion of biochars that are produced from LGB, even after a significant amount of VM was reduced by the carbonization process. We hypothesize that mineral transformation occurs in high-ash biochar during the combustion at higher temperatures and that releases as PM. Therefore, in this study, the emission factor of high ash-containing biochar was investigated at combustion temperatures between 650 to 850 °C. The PM emission from these biochar samples was increased with the increase in combustion temperature. The composition of minerals in the ashes of rice straw, rice husk, and dairy manure was investigated before and after heating at different temperatures (650, 750, and 850 °C). Mineral analysis revealed that enhanced PM emission from ash-rich biochar samples can be attributed to a greater concentration of Na and K and the melting of their compounds at higher combustion temperatures. We also found that co-combustion of low-ash biochar with high alkali-containing biochar may effectively reduce the PM emission, mainly by the mineral dilution mechanism.

3.2. Introduction

The PM emission during the combustion of biomass could reduce by more than 50 percent by carbonization-induced decomposition of organic volatile matter (VM) originating from cellulose, hemicellulose, and lignin (H. Yang et al. 2007; Itoh et al. 2020). The efficiency is highest in the woody biomass, whereas in LGB the reduction is varied depending on the content and composition of inorganic minerals. Especially the alkali minerals including potassium and sodium (K and Na). These are abundant in annual fast-growing plants and translocated as water-solubilized forms from the soil to various parts of the plant (Boström et al. 2012). During the combustion of biomass, alkali minerals (KOH, KCl, K_2SO_4, NaCl, and Na_2SO_4) tend to contribute to the PM by vaporizing easily and forming aerosols in the gas phase (Boström et al. 2012), which could be removed by carbonization below 400 - 500 °C (Z. Hu et al. 2018; Itoh et al. 2020). However, after biomass carbonization along with fixed carbon enrichment, other crystalline species of K and Na could be increased and decomposed during combustion as PM once the temperature is above the boiling point of alkali metals.

To lower PM emissions from solid fuels, it is required to reduce the ash alkali minerals in the fuel matrix (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020) and previous studies have suggested two approaches. One is the dilution of minerals in LGB by co-firing high-quality primary biomass to reduce the overall ash content of the fuel (Fagerström et al. 2010; Rebbling et al. 2020). The second is, to add additives (kaolin or other Si-based additives) or co-combustion based on chemical speciation to modify the ash content and composition of the fuel (Mlonka-Mędrala et al. 2020; Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020; Wu Yang, Pudasainee, Gupta, Li, Song, et al. 2020).

Based on research on PM reduction methods using diverse biomass, coal, and some pretreated biomass, Yang et al. proposed that a low $(K_2O+Na_2O)/(SiO_2+Al2O_3)$ ratio in the ash is required to minimize PM emissions during combustion (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). The biomass co-combustion with coal has shown a significant reduction of PM generation by potassium from the biomass could be captured by aluminosilicate oxides of the coal (W. Wang et al. 2019). The main mechanism is that

vaporized alkali minerals (above 759 °C) during the combustion can be adsorbed on the aluminosilicate, once the combustion temperature exceeds the ash fluid temperature which is usually above 950 °C (Kleinhans et al. 2018). Therefore, the adsorption effect by co-combustion only has been proven in higher combustion temperatures of 1200-1700°C (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). However, Niu et al. have reported capsicum straw ashed at 815 °C has formed zeolite and leucite by following the reaction through R 1, and R 2.

$2KCl + Al_2O_3 + 2SiO_2 + H_2O \rightarrow 2KAlSiO_4 + 2HCl\uparrow$ (R1)

$2KCl + Al_2O_3 + 4SiO_2 + H_2O \rightarrow 2K(AlSi_2O6) + 2HCl\uparrow$(R2)

To assess the application of the co-combustion study it is necessary to examine the mineral composition of the feedstock and test the lower combustion temperatures as the conventional stove operates. Except for a few studies of torrefied biomass co-combusted with coal or water leaching treatments (W. Wang et al. 2019; Han et al. 2019), there are no studies on methods of PM emission reduction from biochar combustion. Therefore, examining the various strategies to reduce PM emission from biochar produced from LGB is required to increase waste utilization. To reduce the emission of PM from the mineral part of biochar, the present study hypothesized that, reducing the K and Na content in the high ash biochar will suppress the PM emission during combustion at lower than the 850°C.

3.3. Materials and methods

3.3.1. Materials

Rice straw (RS), rice husk (RH), dairy manure (DM), and Japanese larch (JL) samples were collected from the experimental farm of Hokkaido University, Sapporo, Japan. To remove the inherent moisture, feedstocks were dried at 105 °C for 24 h, then milled and sieved through a 0.5-mm sieve prior to carbonization. Biochar samples were produced by carbonization of the biomass at 400 °C for 1 h in a FO810 muffle furnace (Yamato Scientific, Tokyo, Japan). Biochar samples were designated as RSB, RHB, DMB, and JLB where “B” indicates the biochar sample. For the co-combustion experiment, biochar samples are divided into two batches as described in the table-2 for determining the effect

of adsorption and diluting effect. Before the co-combustion experiment, the biochar samples were ground using mortar and pestle for better homogenizing the samples.

Batch-1 was designated for testing the adsorption effect of alkaline minerals in biochar by co-combustion with RHB, which may improve the ratio of SiO_2+Al_2O_3 content in biochar co-combusted with DMB and RSB, both of which have significant K_2O+Na_2O content.

Batch-2 was designated for checking the dilution effect of alkaline minerals in biochar by decreasing the ash content of the biochar samples by co-combust with JLB which contains only 1% of ash.

Table 3-3 The mixing ratio of the biochar

No	Designation	RHB (g)	DMB (g)	RSB (g)	JLB (g)	
1	RHB	0.5	-	-	-	Pure biochar
2	DMB	-	0.5	-	-	
3	RSB	-	-	0.5	-	
4	JLB	-	-	-	0.5	
8	RHB1: RSB3	0.125	-	0.375	-	Batch -1
9	RHB1: RSB1	0.25	-	0.25	-	
10	RHB3: RSB1	0.375	-	0.125	-	
11	RHB3: DMB1	0.375	0.125	-	-	
12	RHB1: DMB1	0.25	0.25	-	-	
13	RHB3: DMB1	0.125	0.375	-	-	
14	JLB1: RSB3	-	-	0.375	0.125	Batch -2
15	JLB1: RSB1	-	-	0.25	0.25	
16	JLB3: RSB1	-	-	0.125	0.375	
17	JLB3: DMB1	-	0.125	-	0.375	
18	JLB1: DMB1	-	0.25	-	0.25	
19	JLB3: DMB1	-	0.375	-	0.125	

3.3.2. PM emission measurements

PM emission factor

To validate the combustion temperature dependency of PM emission, the emission factor of RSB, and DMB samples were combusted at 650, 700, 725, 750, 775, 800, and 850 °C. To compare the emissions of total suspended PM during the combustion of the pure and

mixed biochar materials described in table 1, the EF of total PM was determined using the equipment described in Chapter 2 (Fig. 2-1). Based on the experimental result of the PM emission factor of the pure biochar samples (RHB, DMB, RSB, JLB) expected PM emission of the mixed biochar samples was estimated.

To evaluate our result in real-world usage, minimum, average, and maximum airflow rates measured in 59 households that use conventional stoves in the ger, the traditional Mongolian dwelling, in the suburbs of Ulaanbaatar, Mongolia was used as an example (Bayartogtokh and Zhang 2019). The PM emission concentration (C [μg/m^3]) was calculated using the following equation.

$$C = k\frac{mP}{Ft}$$

k – unit conversion factor [=10^3]

m – fuel mass [g-fuel]

P – PM emission factor [mg-PM/g-fuel]

F –air flow rate [m^3/h]

t – measurement time [h]

To observe the temporal variation in the $PM_{2.5}$ emission rate was measured at a combustion temperature of 850 °C using the PM emission sensor developed by Nakayama et al., (Nakayama, Matsumi, and Kawahito & Yoshifumi Watabe 2018) in the system shown in Fig. 3-1. The mass concentration of $PM_{2.5}$ was measured at 10-s intervals in the sensor which was placed in the middle of the sensor box. The emission rate has been evaluated as Itoh et al., introduced (Itoh et al. 2020).

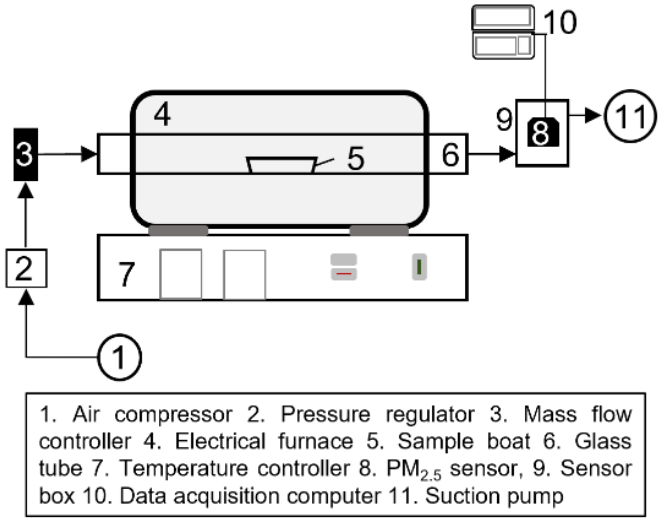


Fig. 3-1 Furnace design and experimental setup of PM emission rate

3.3.3. Mineral content analysis

To determine minerals that could contribute to PM emissions, ash samples of RH, RS, and DM were produced by the incineration of those biomasses at 600 °C. After the samples were incinerated, 300 mg of each ash sample was heated at 650, 750, or 850 °C for 60 min in a tube furnace. The products are referred to as heated ash samples.

The mineral (Al, Ca, K, Mg, Na, P, and Fe) content in the samples (in the ash, heated ash, and biochar) was determined by inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer, Waltham, MA, USA). Before the analysis, samples were digested by an HNO_3 – H_2O_2 system, and the liquid fraction was analyzed by ICP-MS. The solid fraction after the digestion, which was dominated by crude silica [37], was collected by filtration and then weighed after drying.

3.3.4. Statistical analysis

A one-way analysis of variance (ANOVA) was performed within the RSB and DMB samples shown in Figure 3-2 using IBM SPSS (version 28) statistics to determine if there was a statistically significant difference between the emission factors at different combustion temperatures. Tukey's test was used to determine if a significant difference ($p < 0.05$) existed in the PM emission factor analysis within the same biochar or the K and Na content analysis. A correlation test and t-test ($p < 0.05$) were conducted to compare the experimental result and the expected result.

3.4. Results and discussion

3.4.1. PM emission combustion temperature dependency

To verify the PM emission factor in various temperatures, high ash containing biochar RSB and DMB has been combusted in various temperatures ranging from 650 to 850 °C as shown in Fig.3-2. PM emission of DMB has significantly increased in combustion temperature 750 °C compared with the value of lower temperature range. The emission has reached its highest point at 775 °C and has not found a significant change in the above temperatures. In RSB samples, the emission has shown steadily increased up to 775 °C of combustion temperature and the highest emission factor has been recorded. It is observed that in both samples highest emission factor is recorded in the 775°C.

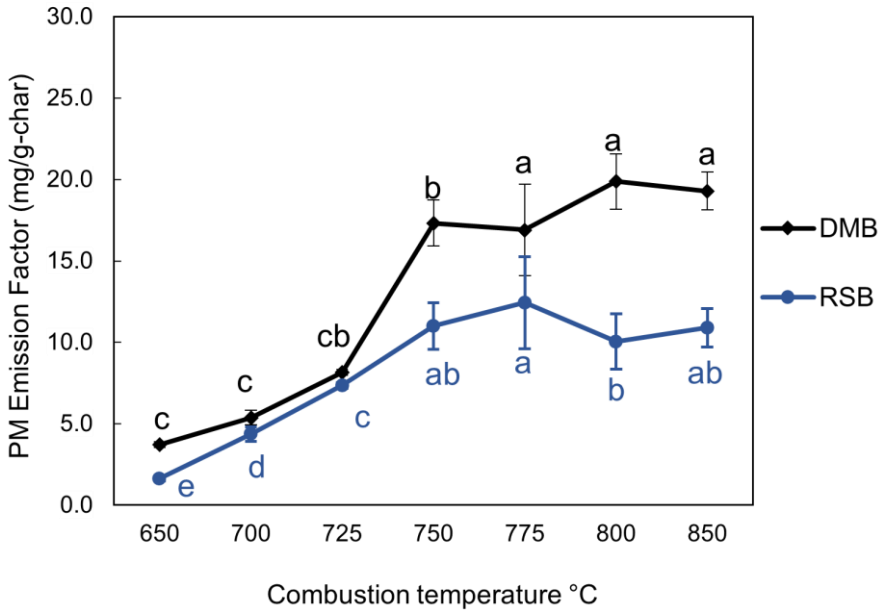


Fig. 3-2 PM emission of dairy manure and rice straw biochar samples at various combustion temperatures [values are mean±standard deviation of three replicates; values with different superscripts within the same biochar group were significantly different, as determined by Tukey's test (p<0.05)]

3.4.2. Mineral composition analysis

3.4.2.1 Ash composition

To elucidate the mechanism of PM emission from the ash samples RH, RS, and DM samples were subjected to ash heating and fractionation analysis. The mass loss due to the heating of the ash samples is depicted in Fig. 3-3a. 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. 3-3b. 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 content and 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.

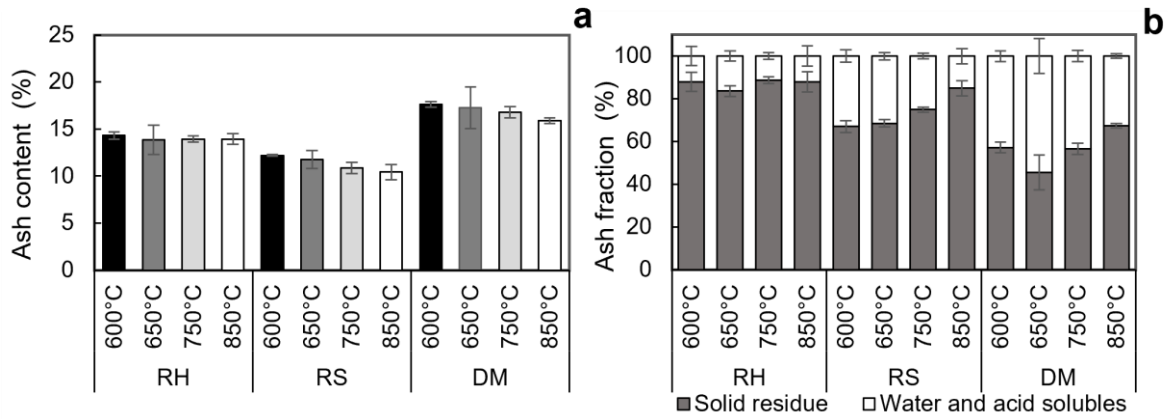


Fig. 3-3 (a) Ash content (%) and (b) solid and insoluble fractions in ash and heated ash of rice husk (RH), rice straw (RS), and dairy manure (DM).

The ash of RS and RH are both dominated by Si (94.7% and 73.2%, respectively); however, RS has higher contents of alkali and alkaline-earth metals (Yao, Xu, and Liang 2016). The total content of Al, Ca, K, Mg, Na, P, and Fe in the RH, RS, and DM have shown in appendices 1-3. RH leachates were significantly lower than the RS and DM leachates. The dominant soluble species in the ash sample of RH were K, Fe, and P (5.8, 1.9, and 1.3 mg/g, respectively)). There was no significant difference in the concentration of ash minerals between the ash and heated ash samples of RH (Fig. S1).

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 (Fig. S2) than the RH. The concentration of other elements was 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) (Fig. S3). There is a significant reduction of K content in both RS and DM ashes when increasing the heating temperature.

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 (Beidaghy Dizaji et al. 2022). 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 (the main soluble minerals) remaining after the ash samples were heated at higher temperatures (Table 3-2).

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 might have been released as PM increased with increasing heating temperature. The same phenomenon was observed in a previous study (Itoh et al. 2020).

Table 3-4 K and Na content of ash and heated ash samples

SAMPLE	**K (mg/g)**			**Na (mg/g)**		
	RH	RS	DM	RH	RS	DM
ASH	5.8±0.04^{a}	51.1±8.88^{a}	96.8±4.73^{a}	0.1±0.00^{c}	0.5±0.01^{a}	17.3±0.79^{a}
650 °C	5.4±0.08^{b}	61.1±1.51^{a}	94.6±4.32^{a}	0.1±0.01^{c}	0.5±0.01^{a}	18.6±0.88^{a}
750 °C	4.9±0.11^{c}	19.2±1.81^{b}	62.3±3.57^{b}	0.2±0.01^{b}	0.4±0.00^{b}	14.1±0.72^{b}
850 °C	5.9±0.07^{a}	1.3±0.18^{c}	19.4±1.07^{c}	0.25±0.01^{a}	0.15±0.01^{c}	9.5±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 3-2). The increased emission factor of the RSB and DMB, and the reduction of alkali mineral concentration above 750°C. 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.

3.4.2.2 PM emission and mineral composition

To reduce the PM emission, the alkali-metal content in biomass and coal has been suggested (Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). To confirm this speculation in the case of biochar, 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. 3-4, at combustion temperatures of 750 and 850 °C, the PM EF of high-ash biochar 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 and alkaline-earth metals occurs either below 500 °C or above 800 °C (Weber and Quicker 2018). Sublimation of KCl could be the main path of K release (Spokas et al. 2014). 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.

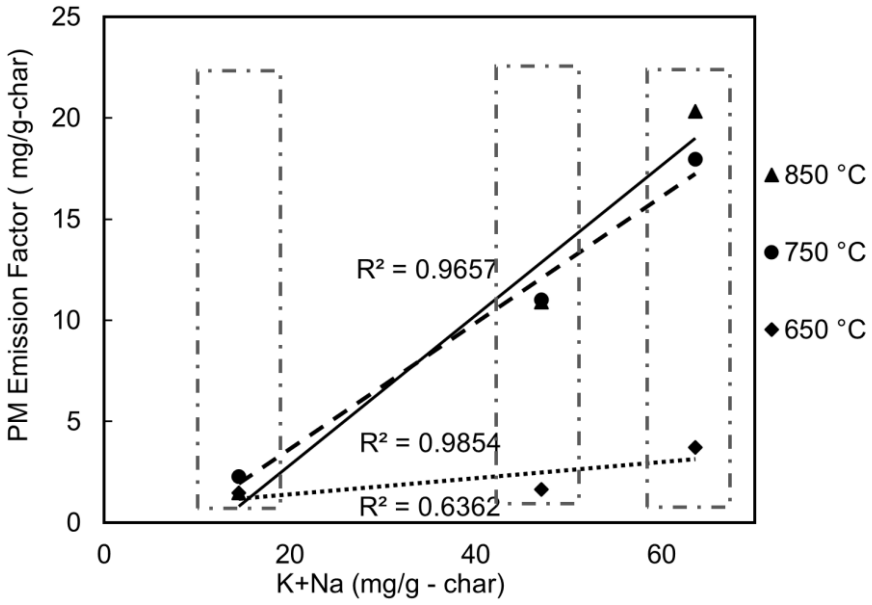


Fig. 3-4 Correlation of the alkali-metal content and PM EF for rice husk, rice straw, and dairy manure biochar

3.4.3. PM emission behavior of co-combustion

3.4.3.1 PM Emission factor

Table 3-3 shows the measured emission factor of PM from pure and mixed biochar samples to limit the emission of PM from ash. The emission of PM has reduced when increasing the content of the high Si and Al-containing RHB part in the combustion mixture as well as the increase of the low ash-containing JLB. The emission factor of JLB is lower than that of RHB, therefore the co-combustion with JLB was mostly effective than co-combustion with RHB.

Table 5-3 PM EF of the pure and co-combusted biochar of

No	Mixing ratio	PM Emission factor (mg/g)	
1	RHB	2.0 ± 0.1	Pure biochar
2	DMB	21.2 ± 1.2	
3	RSB	11.3 ± 0.7	
4	JLB	1.0 ± 0.6	
8	RHB1: RSB3	9.4 ± 0.3	Batch -1
9	RHB1: RSB1	5.7 ± 0.2	
10	RHB3: RSB1	3.4 ± 0.7	

11	RHB1: DMB3	16.4 ± 0.6	
12	RHB1: DMB1	10.0 ± 0.4	
13	RHB3: DMB1	5.3 ± 1.0	
14	JLB1: RSB3	8.4 ± 1.3	Batch -2
15	JLB1: RSB1	6.2 ± 0.1	
16	JLB3: RSB1	2.8 ± 0.6	
17	JLB1: DMB3	10.7 ± 1.0	
18	JLB1: DMB1	9.9 ± 0.8	
19	JLB3: DMB1	6.1 ± 0.5	

In Fig. 3-5 the correlation between the molar ratio of $(K_2O+Na_2O)/(SiO_2+Al_2O_3)$ and the measured PM emission factor of mixed biochar samples is shown. The emission factor of the PM was highly correlated with the ratio of $(K_2O+Na_2O)/(SiO_2+Al_2O_3)$ content in ash. The content of Si and Al content was highest in the RHB, and EF was many folds lesser than the DMB and RSB. However, we did not find a significant difference between the predicted and the experimental data of EF measurement (Fig. 3-6). That indicates the dilution effect rather than the adsorption effect by the $SiO_2+Al_2O_3$ in the ash component may have led to a reduction in PM emissions.

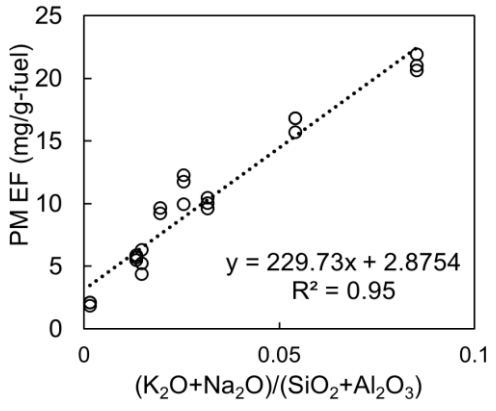


Fig. 3-5 Correlation of the emission factor of PM and $(K_2O+Na_2O)/(SiO_2+Al_2O_3)$ of batch 1

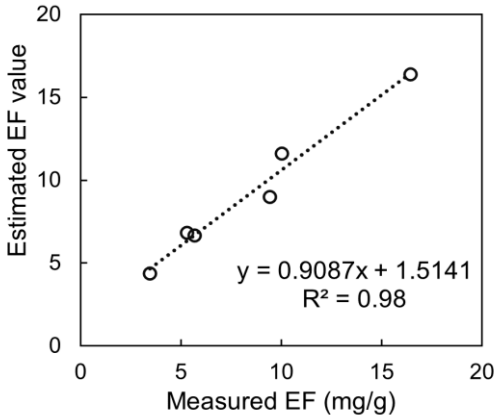


Fig. 3-6 The correlation of PM EF of batch 1, the experiment, and the estimated value based on the pure biochar EF

3.3.3.2 Emission rate of the PM

To examine the behavior of PM emission further, the real-time emission rate of PM was measured by burning DMB, the most PM-emitting biochar, with RHB and JLB. The

emission during the combustion of RHB has shown the highest peak within five minutes and the emission has been eliminated. Whereas the dairy manure biochar sample has shown a significantly different trend after the emission peaked and retarded within 5 minutes another peak has been formed. In a different study, when torrefied dairy manure was combusted at 850 °C, a similar two-peaked pattern was observed, but not at 650 °C (Itoh et al. 2020). The combustion of raw biomass results in the degradation of organic materials, whereas carbonization is intended to reduce the organic element of the biomass. However, lignin, one of the main organic components of biomass, has a wide decomposition temperature range of up to 530 °C (Glushkov et al. 2021; H. Yang et al. 2007). This indicates that the first peak could be caused by delayed lignin breakdown. The observed second peak of the DMB, on the other hand, could be caused by ash transformation after char combustion and smoldering (Itoh et al. 2020).

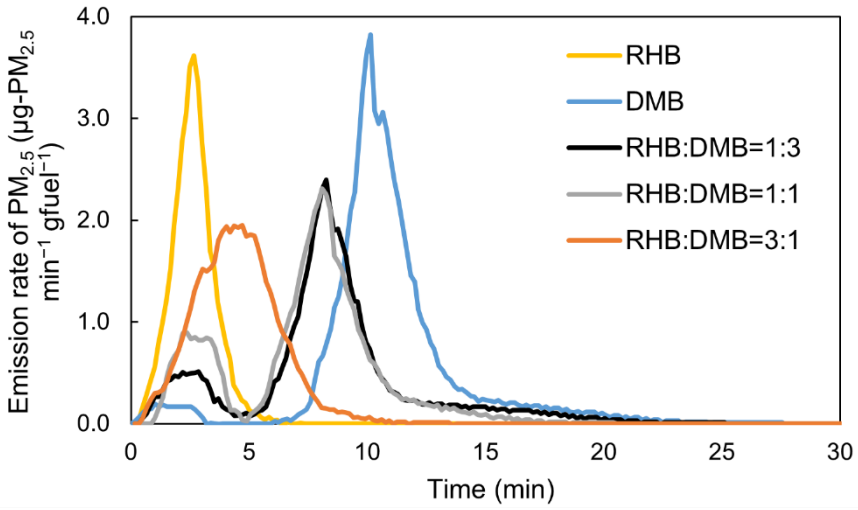


Fig. 3-7 PM emission rate of DMB with co-combustion of RHB

When the amount of RHB mixing ratio is equal to or less than the DMB in co-combustion, the emission trend follows a similar two-peaked pattern. Whereas the RHB and JLB-dominated (3:1) treatment has changed the emission trend of the fuel by eliminating the second peak. Therefore, the K_2O+Na_2O adsorption by SiO_2+Al_2O_3 could occur when the mixing ratio of the RHB is 3 times more than the DMB. However, the JLB-dominated co-combustion also showed a similar trend therefore further synergistic effects of the co-combusted biochar may have occurred. For instance, woody biomass contains a high amount of Ca which forms a K_2CO_3–$CaCO_3$ melt around 800 °C resulting in reduced release of K (Hedayati et al. 2021).

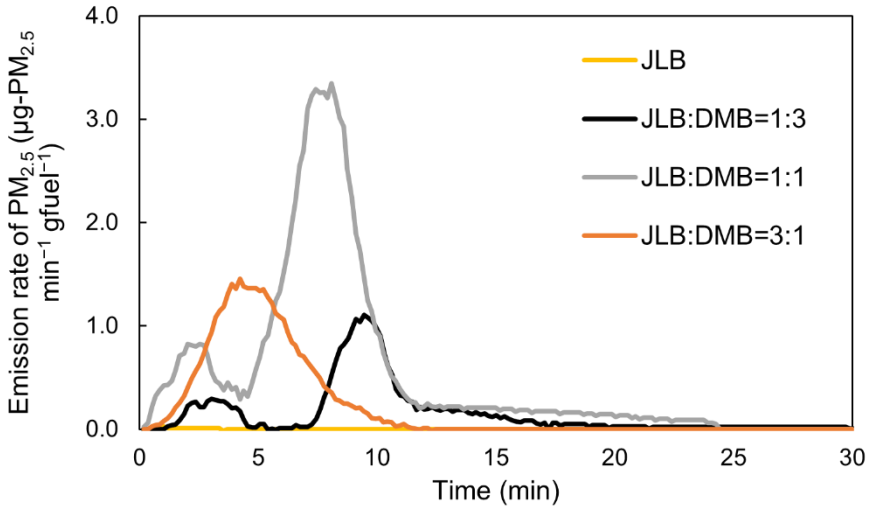


Fig. 3-8 PM emission rate of DMB with co-combustion of JLB

As shown in Fig. 3-9 there is almost no difference between all the co-combusted biochar (both batch 1, 2) emission factors and estimated value. Therefore, the emission of PM from the mineral part of biochar samples can be reduced by co-combustion of the biochar based on ash content.

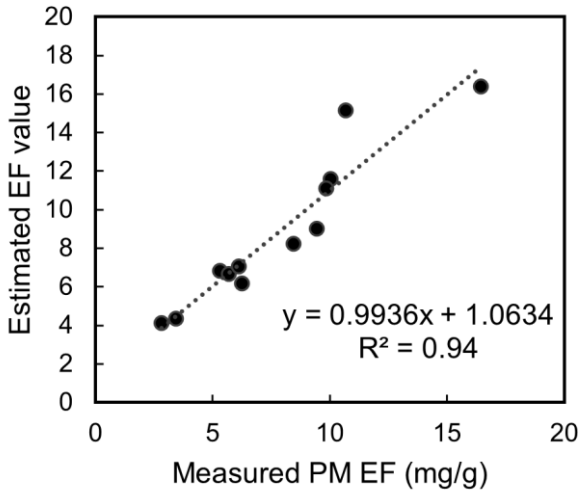


Fig. 3-9 Correlation of estimated and measured EF co-combustion of batch 1, 2 biochar

The emission rate targets for mitigating PM exposure in a household, WHO air quality guideline for $PM_{2.5}$ of the vented stove was 0.80 mg/min, and 7.15 mg/min in the ultimate and intermediate targets respectively (WHO 2021). In our study emission rate of biochar ranged between 0.0 to 4 mg/min. This indicates that the emission of PM from biochar combustion is expected to qualify for the emission target. However, in this study, the

emission rate did consider an energy-delivered factor of emission as WHO estimation has suggested. Therefore, to measure the emission rate considering the factor of energy delivered value, further study needs to consider the field measurement of air exchange rate/ventilation rate, kitchen volume, and duration of stove use per day.

3.4.4. Comparison of PM emission concentration and WHO guidelines

Fig. 3-10 compares the PM emission concentration computed based on the PM emission factor of the pure and mixed biochar we measured with three alternative airflow rates available in the literature (Bayartogtokh and Zhang 2019), to the WHO air quality guideline 24-hour mean ($PM_{2.5}$ – 15 µg/m^3; PM_{10} – 45 µg/m^3) (WHO 2021). It was observed that the JLB and RHB have emitted PM lower than the WHO guideline. However, since airflow rate is another important factor in PM emission concentration, more research is needed to examine the airflow rates of stoves more carefully. The co-combustion of the JLB with high ash-containing biochar has shown a promising effect in reducing the emission of PM, especially when the airflow rate is sufficient. The PM emission reduction was observed more in RSB than in DMB co-combusted with JLB. Because the ash content of RSB is lower than the DMB. Therefore, by reducing the PM emission from high ash-containing biochar by co-combustion, reducing the overall ash content in the mixture could be expected a better result.

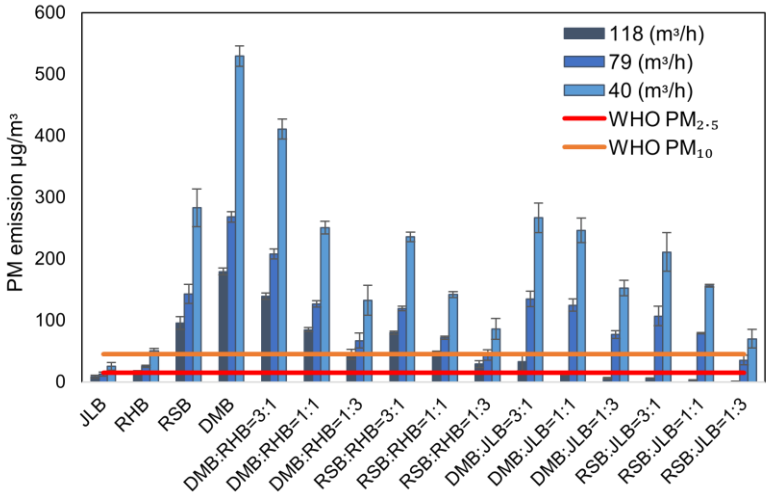


Fig. 3-10 PM emission concentration of pure and mixed biochar

3.5.Conclusion

The emission of the PM from the ash part has been greatly influenced by the combustion temperature and composition of the feedstock that is used for biochar production. The emission of PM from RSB and DMB was increased significantly in the combustion temperature range of 725 to 775 °C. The emission was stabilized later, or a slight decrease was observed between 775-850 °C. Emission from the alkali-metal content in the ash was the main reason for elevated PM emission of biochar samples at higher combustion temperatures. As our study proved that the PM emission from co-combustion biochars can be predicted quite accurately, this model can be utilized to design various combinations of biochar-based solid fuel that would satisfy the WHO emission guideline.

CHAPTER – 4. GENERAL DISCUSSION AND RECOMMENDATIONS

4.1. Biomass type on PM generation

Biomass is the most abundantly available renewable resource (Liu, Jiang, and Yu 2019). Therefore, the carbonization of biomass material is a viable solution for addressing numerous concerns, such as increasing clean renewable energy supply and minimizing waste as part of the circular economy (Q. Hu et al. 2021). However, its use as a solid fuel remains understudied (Kant Bhatia et al. 2021), and even the prospect of lowering PM emissions is promising. Therefore, this study has demonstrated the PM emission reduction effect of various biomass by carbonization.

Based on the review study results of the life cycle assessment of a wide variety of biochar, Zhu et al concluded that the increasing environmental advantages biochar production process should adapt to local or regional level (X. Zhu et al. 2022). Therefore, the tested biomass in this study were selected based on the abundance and low utilization options. The PM emission during the combustion of selected seven types of biomasses and their carbonized types were compared to evaluate the efficiency of PM reduction and the influencing factors.

In this study, PM emissions have been reduced significantly from all biochar due to the removal of the volatile matter by carbonization. The average PM emission from the biochar was lowest in woody biochar and energy coppices (PoB < MiB < JLB< RHB < BGB < RSB < DMB). The countries that have a high abundance of forest residue, i.e, Mongolia, the carbonization of poplar wood or larch would be beneficial. Further, effective forest management, thinning and forest floor cleaning from dead wood and log is generally suggested (Altrell 2019). The broad-leaf bamboo is an invasive species in the northern temperate forest of Japan. Removal of the invasive plant is effective silvicultural prescription to sustain overstory plant diversity (Ishii et al. 2008), so plants like bamboo grass can be carbonized and utilized as biosolid fuel. As a result, active utilization of this kind of biomass materials would help maintain a healthy sustainable forest ecosystem.

Given that rice, meat, and dairy products are the staple diet for billions of people, food processing waste would increase year after year. The residual biomass from the agricultural activity is typically either burned in the agricultural field or discarded as waste, both of which pollute the environment. Consequently, effective utilization of such

biomass is gaining more attention. Therefore, unutilized biomass resource surveys in the country or region and their compositional study would assist in the sustainability of biomass utilization and its emission prediction of PM during combustion.

4.2. PM emission behavior

Fuel properties including fuel particle size, mineral properties, inherent ash content, and its composition are big factors for PM emission quantity accompanying furnace design (Leskinen et al. 2014; Sun et al. 2019; Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). Therefore, the PM emission behavior and reduction possibility based on the mineral composition and combustion temperature has been evaluated. The main source of PM emission from biomass is due to the VM of organic parts as reviewed in the literature (Van Loo and Koppejan 2008; Basu 2013). We found that a substantial amount of PM is also emitted from the inorganic part. Combustion temperature has a significant impact on PM emission from high ash-containing biomass (≥6.7%). As our hypothesis, the PM emission reduction results show that the emission has been reduced significantly by carbonization from all the biomass at low combustion temperatures.

The results from the first phase of the study, suggest that the PM emission from the ash-rich biochar is highly dependent on its composition and combustion temperature. Most of these ash-rich biochars are produced from LGB. Finding an effective way to utilize carbonized LGB as a solid fuel without many emissions will have a significant impact on renewable energy research and the well-being of the rural community in many developing countries

Therefore, detailed combustion temperature and ash mineral components of high ash-containing biochar were investigated relating to the emission of PM during combustion. Based on the first phase of the study results, we hypothesized that mineral transformation occurs in high-ash biochar during the combustion at higher temperatures and that releases as PM. The ash composition of the high ash-containing biochar samples namely rice husk (RHB), rice straw (RSB), and dairy manure biochar (DMB) were analyzed.

The emission of PM from RSB and DMB was increased significantly with combustion temperature increase. The highest PM emitting range was well aligned with the studies

that stated the release of alkali minerals could occur at 700 to 900 °C during combustion (Jensen, Sander, and Dam-Johansen 2001; Yogalakshmi K N et al. 2022). Further, the ash composition and the heating study revealed that the RH, RS, and DM include 12.1%, 32.6%, and 42.8% of soluble minerals, respectively. The insoluble part of the ash is mainly consisting of Si and other refractory or acidic compounds whereas the soluble part of the minerals is mostly alkaline and alkaline earth minerals including K_2O, CaO, Na_2O, etc. The high emission of PM owing to high heating temperature is influenced by alkali metal release from the soluble ash part of RS and DM. The heating temperature of the RS and DM ash increased, and the soluble portion of the ash decreased. The decrease in the ash soluble part was due to the degradation of a significant amount of K and a small amount of Na. As our hypothesis, the PM EF of high-ash biochar was strongly correlated with their K+Na content when the combustion temperature was higher.

Compared to biochars with higher ash content, RHB differed most in terms of ash chemical composition, and PM emission behavior. The low emission from RHB is due to the high percentage of insoluble mineral Si. It is known that rice husk ash has a high content of SiO_2 (Wei Yang et al. 2017), which is considered a favorable fuel additive for reducing alkali metals. Therefore, considering its lower PM emissions, RHB might be employed as a solid fuel. However, due to the possibility of slagging, the sample's high ash concentration may impede its use (Dunnigan et al. 2018; Yao, Xu, and Liang 2016). Therefore, the reduced ash content of RHB would make this biochar more valuable as solid fuel.

To reduce the emission of PM induced by the alkaline mineral content we tested two approaches as literature supported (Mlonka-Mędrala et al. 2020; Wu Yang, Pudasainee, Gupta, Li, Wang, et al. 2020). The high PM emitting RSB and DMB high-alkaline-ash biochar was co-combusted with low-ash JLB to dilute ash minerals. Additionally, those were co-combusted with high Si-containing RHB to test the adsorption effect. From the co-combustion study, it was observed that the emission reduction by ash dilution is more likely to happen than the adsorption effect, since the batch 1, and 2 studies both well correlated with the expected results of emission reduction. The adsorption effect has not occurred might because the combustion temperature was below the Si melting temperature and the Al content was not high enough. Since the co-combusted materials

were not pure additives, more complex ash transformation may have occurred. Nevertheless, the co-combustion based on the ash content of the biochar can be applied to reduce the emission of PM during the combustion of the biochar in the various ranges of conventional stove temperature.

4.3. Conclusive summary

From overall results and discussion, we conclude that carbonization is effective in reducing PM emissions from low ash-containing biomass, or low alkali-containing biochar in combustion temperatures of 650-850 °C. The high-alkali-containing biochars can be combusted at 650°C. For combustion above that temperature, ash content should be diluted to reduce the emission of PM. The comparison of probable PM release rate and WHO emission concentration guidelines have shown the possibility to use the LGB as a potential bio-solid fuel (with reduced PM emission). Based on the preceding findings, the flowchart below is provided to assist in further biomass upgrading and predicting the effectiveness of carbonization to reduce PM emissions during combustion (Fig. 4-1).

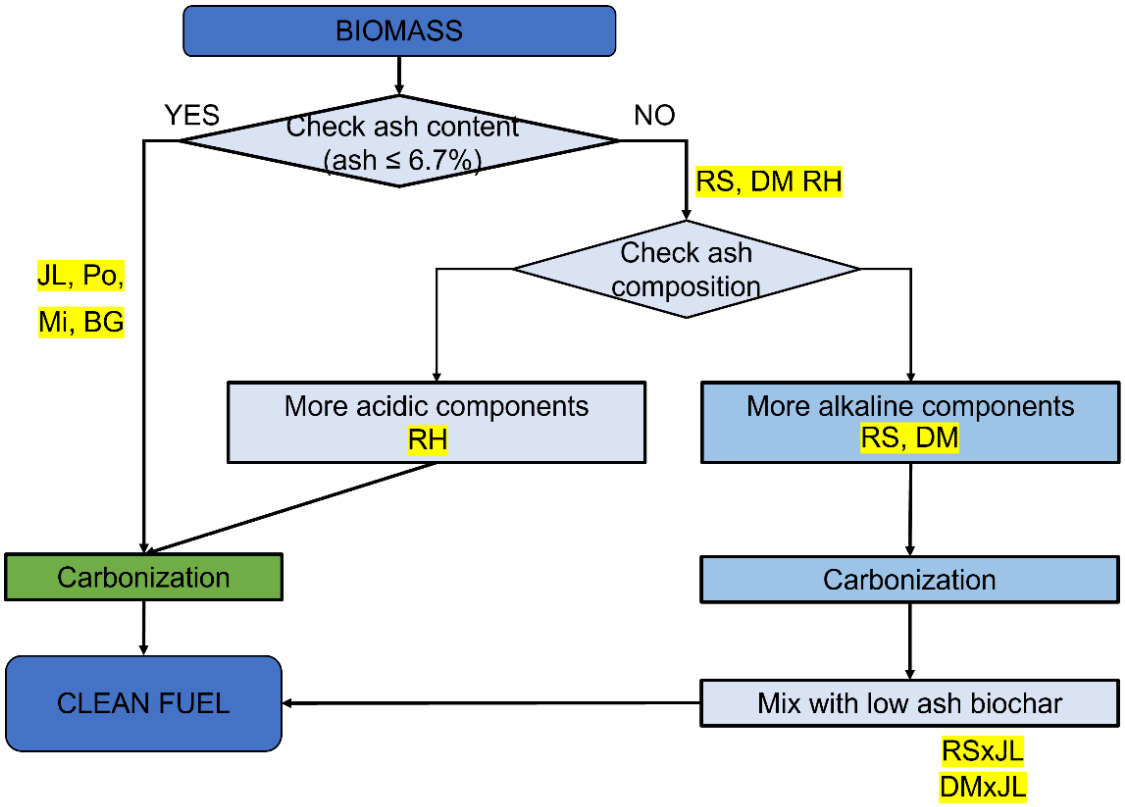


Fig. 4-1 Diagrammatic outline of producing clean biosolid fuel by carbonization

4.4. Study limitations and suggestions for future research

As our study has mainly focused on environmental factors of biochar, future study needs to evaluate the commercial and technical value of biochar as solid fuel as follows.

- For further studies, it is necessary to examine the fuel particle size effect on the PM emission factor. Because, when the emission factors of the RHB, RSB, and DMB were compared in the second and third chapters of the study, a modest rise was noticed in chapter 2, although the combustion conditions were the same. The difference may be occurred due to the biochar particle size since the second part of the study, biochar samples were ground to finer sizes.
- To assess biochar fuel production and ease of future utilization, the biochar mechanical densification method including briquette/pelletizing (a technique to harden and bind a material by compressing under high pressure) may be beneficial. Various studies have suggested that the densification of biomass and coal has been effective to reduce PM emissions along with increasing energy density and overall fuel quality (Y. Zhu et al. 2018; Sun et al. 2019).
- It is necessary to perform a field combustion experiment to evaluate whether the emission reduction target is achievable in a real environment, regarding different ventilation rates and firing behavior of the user for instance the average cooking time.
- Considering the mineral composition heterogeneity, and possible melting of the Ca-Mg-Si-P-O system (Falk et al. 2022) during the co-combustion of biochar, the emission of PM prediction could be assisted by ternary composition diagram of biomass ash introduced by Vassilev et al. (2017).
- More precise PM emission prediction models should be developed
- Evaluation of lower heating and higher heating value of the biochar is necessary to estimate the commercial value of biochar as fuel.

REFERENCES

Abah, Emmanuel Owoicho, Tofael Ahamed, and Ryozo Noguchi. 2020. “Investigative Study for Low Particulate Matter Emission in Rice Husk Combustion.” *Journal of the Japan Institute of Energy* 99 (11): 220–29. https://doi.org/10.3775/jie.99.220.

ADB. 2019. “Report No : PAD2929.”

Agency, International Energy. 2022. “International Energy Agency (IEA) World Energy Outlook 2022.” *Https://Www.Iea.Org/Reports/World-Energy-Outlook-2022/Executive-Summary*.

Altrell, Dan. 2019. “Multipurpose National Forest Inventory in Mongolia, 2014-2017-a Tool to Support Sustainable Forest Management.” *Geography, Environment, Sustainability* 12 (3): 167–83. https://doi.org/10.24057/2071-9388-2019-36.

Basu, Prabir. 2013. *Biomass Gasification, Pyrolysis and Torrefaction : Practical Design and Theory*. 2nd ed. Amsterdam: Academic Press. https://opac.lib.hokudai.ac.jp/opac/opac_link/bibid/2001666042 CN - Agriculture, Library 662.88/B293 CN - Agriculture, Library 662.88/B293 CN - Agriculture, Library 662.88/B293.

Bayartogtokh, Bilguun, and Qingyuan Zhang. 2019. “ウランバートルにおけるゲルの冬季室内熱環境の調査.” 日本建築学会環境系論文集 84 (757): 245–53. https://doi.org/10.3130/aije.84.245.

Beidaghy Dizaji, Hossein, Thomas Zeng, Hieronymus Hölzig, Jens Bauer, Gert Klöß, and Dirk Enke. 2022. “Ash Transformation Mechanism during Combustion of Rice Husk and Rice Straw.” *Fuel* 307 (April 2021). https://doi.org/10.1016/j.fuel.2021.121768.

Boström, Dan, Nils Skoglund, Alejandro Grimm, Christoffer Boman, Marcus Öhman, Markus Broström, and Rainer Backman. 2012. “Ash Transformation Chemistry during Combustion of Biomass.” In *Energy and Fuels*, 26:85–93. UTC. https://doi.org/10.1021/ef201205b.

Broer, Karl M., and Robert C. Brown. 2015. “The Role of Char and Tar in Determining the Gas-Phase Partitioning of Nitrogen during Biomass Gasification.” *Applied Energy* 158: 474–83. https://doi.org/10.1016/j.apenergy.2015.08.100.

Bruce, Nigel, Dan Pope, Eva Rehfuess, Kalpana Balakrishnan, Heather Adair-Rohani, and Carlos Dora. 2015. “WHO Indoor Air Quality Guidelines on Household Fuel Combustion: Strategy Implications of New Evidence on Interventions and Exposure-Risk Functions.” *Atmospheric Environment* 106 (April): 451–57. https://doi.org/10.1016/j.atmosenv.2014.08.064.

Burhenne, Luisa, Jonas Messmer, Thomas Aicher, and Marie-Pierre Laborie. 2013. “The Effect of the Biomass Components Lignin, Cellulose and Hemicellulose on TGA and Fixed Bed Pyrolysis.” *Journal of Analytical and Applied Pyrolysis* 101 (May): 177–84. https://doi.org/10.1016/j.jaap.2013.01.012.

Chen, Dengyu, Anjiang Gao, Kehui Cen, Jie Zhang, Xiaobing Cao, and Zhongqing Ma. 2018. “Investigation of Biomass Torrefaction Based on Three Major Components: Hemicellulose, Cellulose, and Lignin.” *Energy Conversion and Management* 169 (May): 228–37. https://doi.org/10.1016/j.enconman.2018.05.063.

Dunnigan, Lewis, Peter J. Ashman, Xiangping Zhang, and Chi Wai Kwong. 2018. “Production of Biochar from Rice Husk: Particulate Emissions from the Combustion of Raw Pyrolysis Volatiles.” *Journal of Cleaner Production* 172 (January): 1639–45. https://doi.org/10.1016/j.jclepro.2016.11.107.

Enkhbat, Undarmaa, Ana M. Rule, Carol Resnick, Chimedsuren Ochir, Purevdorj Olkhanud, and D’Ann L. Williams. 2016. “Exposure to PM2.5 and Blood Lead Level in Two Populations in Ulaanbaatar, Mongolia.” *International Journal of Environmental Research and Public Health* 13 (2): 1–11. https://doi.org/10.3390/ijerph13020214.

Erni, Matthias, Vanessa Burg, Leo Bont, Oliver Thees, Marco Ferretti, Golo Stadelmann, and Janine Schweier. 2020. “Current (2020) and Long-Term (2035 and 2050) Sustainable Potentials of Wood Fuel in Switzerland.” *Sustainability* 12 (22): 9749. https://doi.org/10.3390/su12229749.

Fagerström, J, I Näzelius, D Boström, M Öhman, and C Boman. 2010. “Reduction of Fine Particle- and Deposit Forming Alkali by Co-Combustion of Peat with Wheat Straw and Forest Residues.” *Proceedings of the Conference Impacts of Fuel Quality on Power Production and Environment*, no. September.

Falk, Joel, Thomas Karl Hannl, Nils Skoglund, Rainer Backman, and Marcus Öhman. 2022. “Thermodynamic Equilibrium Study on the Melting Tendency of the K-Ca-Mg-P-Si-O System with Relevance to Woody and Agricultural Biomass Ash Compositions.” *Energy and Fuels* 36 (13): 7035–51. https://doi.org/10.1021/acs.energyfuels.2c00785.

Fitzpatrick, E. M., A. B. Ross, J. Bates, G. Andrews, J. M. Jones, H. Phylaktou, M. Pourkashanian, and A. Williams. 2007. “Emission of Oxygenated Species from the Combustion of Pine Wood and Its Relation to Soot Formation.” *Process Safety and Environmental Protection* 85 (5 B): 430–40. https://doi.org/10.1205/psep07020.

Garland, Charity, Samantha Delapena, Rajendra Prasad, Christian L’Orange, Donee Alexander, and Michael Johnson. 2017. “Black Carbon Cookstove Emissions: A Field Assessment of 19 Stove/Fuel Combinations.” *Atmospheric Environment* 169: 140–49. https://doi.org/10.1016/j.atmosenv.2017.08.040.

Gill-Wiehl, Annelise, Tom Price, and Daniel M. Kammen. 2021. “What’s in a Stove? A Review of the User Preferences in Improved Stove Designs.” *Energy Research and Social Science* 81 (August): 102281. https://doi.org/10.1016/j.erss.2021.102281.

Glushkov, Dmitrii, Galina Nyashina, Anatolii Shvets, Amaro Pereira, and Anand Ramanathan. 2021. “Current Status of the Pyrolysis and Gasification Mechanism of Biomass.” *Energies* 14 (22). https://doi.org/10.3390/en14227541.

Han, Jingkun, Dunxi Yu, Xin Yu, Fangqi Liu, Jianqun Wu, Xianpeng Zeng, Ge Yu, and

Minghou Xu. 2019. “Effect of the Torrefaction on the Emission of PM10 from Combustion of Rice Husk and Its Blends with a Lignite.” *Proceedings of the Combustion Institute* 37 (3): 2733–40. https://doi.org/10.1016/j.proci.2018.07.011.

Hedayati, Ali, Robert Lindgren, Nils Skoglund, Christoffer Boman, Norbert Kienzl, and Marcus Öhman. 2021. “Ash Transformation during Single-Pellet Combustion of Agricultural Biomass with a Focus on Potassium and Phosphorus.” *Energy and Fuels* 35 (2): 1449–64. https://doi.org/10.1021/acs.energyfuels.0c03324.

Hu, Qiang, Janelle Jung, Dexiang Chen, Ken Leong, Shuang Song, Fanghua Li, Babu Cadiam Mohan, et al. 2021. “Biochar Industry to Circular Economy.” *Science of the Total Environment* 757: 143820. https://doi.org/10.1016/j.scitotenv.2020.143820.

Hu, Zhongfa, Xuebin Wang, Adewale Adeosun, Renhui Ruan, and Houzhang Tan. 2018. “Aggravated Fine Particulate Matter Emissions from Heating-Upgraded Biomass and Biochar Combustion: The Effect of Pretreatment Temperature.” *Fuel Processing Technology* 171 (August 2017): 1–9. https://doi.org/10.1016/j.fuproc.2017.11.002.

Illerup, Jytte Boll, Brian Brun Hansen, Weigang Lin, Joachim Nickelsen, Vagn Hvam Pedersen, Bente Eskerod, and Kim Dam-Johansen. 2020. “Performance of an Automatically Controlled Wood Stove: Thermal Efficiency and Carbon Monoxide Emissions.” *Renewable Energy* 151: 640–47. https://doi.org/10.1016/j.renene.2019.11.057.

Ishii, Hiroaki T, Tsuyoshi Kobayashi, Shigeru Uemura, Koichi Takahashi, Yuko T Hanba, Akihiro Sumida, and Toshihiko Hara. 2008. “Removal of Understory Dwarf Bamboo (Sasa Kurilensis) Induces Changes in Water-Relations Characteristics of Overstory Betula Ermanii Trees.” *Journal of Forest Research* 13 (2): 101–9. https://doi.org/10.1007/s10310-007-0058-0.

Itoh, Takanori, Nana Fujiwara, Kazunori Iwabuchi, Takumi Narita, Dolgormaa Mendbayar, Mitsushi Kamide, Shinobu Niwa, and Yutaka Matsumi. 2020. “Effects of Pyrolysis Temperature and Feedstock Type on Particulate Matter Emission Characteristics during Biochar Combustion.” *Fuel Processing Technology* 204 (July): 106408. https://doi.org/10.1016/j.fuproc.2020.106408.

Jaworek, A., A. T. Sobczyk, A. Marchewicz, A. Krupa, and T. Czech. 2021. “Particulate Matter Emission Control from Small Residential Boilers after Biomass Combustion. A Review.” *Renewable and Sustainable Energy Reviews* 137 (January 2020): 110446. https://doi.org/10.1016/j.rser.2020.110446.

Jensen, P. A., B. Sander, and K. Dam-Johansen. 2001. “Removal of K and Cl by Leaching of Straw Char.” *Biomass and Bioenergy* 20 (6): 447–57. https://doi.org/10.1016/S0961-9534(01)00006-X.

Jia, Yunlu, and Joann S. Lighty. 2012. “Ash Particulate Formation from Pulverized Coal under Oxy-Fuel Combustion Conditions.” *Environmental Science and Technology* 46 (9): 5214–21. https://doi.org/10.1021/es204196s.

Kant Bhatia, Shashi, Akshaya K. Palai, Amit Kumar, Ravi Kant Bhatia, Anil Kumar Patel,

Vijay Kumar Thakur, and Yung Hun Yang. 2021. “Trends in Renewable Energy Production Employing Biomass-Based Biochar.” *Bioresource Technology* 340 (July): 125644. https://doi.org/10.1016/j.biortech.2021.125644.

Kleinhans, Ulrich, Christoph Wieland, Flemming J. Frandsen, and Hartmut Spliethoff. 2018. “Ash Formation and Deposition in Coal and Biomass Fired Combustion Systems: Progress and Challenges in the Field of Ash Particle Sticking and Rebound Behavior.” *Progress in Energy and Combustion Science* 68: 65–168. https://doi.org/10.1016/j.pecs.2018.02.001.

Kortelainen, Miika, Jorma Jokiniemi, Ilpo Nuutinen, Tiina Torvela, Heikki Lamberg, Tommi Karhunen, Jarkko Tissari, and Olli Sippula. 2015. “Ash Behaviour and Emission Formation in a Small-Scale Reciprocating-Grate Combustion Reactor Operated with Wood Chips, Reed Canary Grass and Barley Straw.” *Fuel* 143: 80–88. https://doi.org/10.1016/j.fuel.2014.11.006.

Leskinen, J., J. Tissari, O. Uski, A. Virén, T. Torvela, T. Kaivosoja, H. Lamberg, et al. 2014. “Fine Particle Emissions in Three Different Combustion Conditions of a Wood Chip-Fired Appliance - Particulate Physico-Chemical Properties and Induced Cell Death.” *Atmospheric Environment* 86 (April): 129–39. https://doi.org/10.1016/j.atmosenv.2013.12.012.

Li, Qing, Jingkun Jiang, Qi Zhang, Wei Zhou, Siyi Cai, Lei Duan, Su Ge, and Jiming Hao. 2016. “Influences of Coal Size, Volatile Matter Content, and Additive on Primary Particulate Matter Emissions from Household Stove Combustion.” *Fuel* 182: 780–87. https://doi.org/10.1016/j.fuel.2016.06.059.

Li, Qing, Juan Qi, Jingkun Jiang, Jianjun Wu, Lei Duan, Shuxiao Wang, and Jiming Hao. 2019. “Significant Reduction in Air Pollutant Emissions from Household Cooking Stoves by Replacing Raw Solid Fuels with Their Carbonized Products.” *Science of the Total Environment* 650: 653–60. https://doi.org/10.1016/j.scitotenv.2018.09.020.

Lim, Miyoung, Sainnyambuu Myagmarchuluun, Hyunkyung Ban, Yunhyung Hwang, Chimedsuren Ochir, Delgerzul Lodoisamba, and Kiyoung Lee. 2018. “Characteristics of Indoor Pm2.5 Concentration in Gers Using Coal Stoves in Ulaanbaatar, Mongolia.” *International Journal of Environmental Research and Public Health* 15 (11). https://doi.org/10.3390/ijerph15112524.

Lith, Simone C. van, Violeta Alonso-Ramírez, Peter A. Jensen, Flemming J. Frandsen, and Peter Glarborg. 2006. “Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 1: Development and Evaluation of Quantification Methods.” *Energy and Fuels* 20 (3): 964–78. https://doi.org/10.1021/ef050131r.

Liu, Wu Jun, Hong Jiang, and Han Qing Yu. 2019. “Emerging Applications of Biochar-Based Materials for Energy Storage and Conversion.” *Energy and Environmental Science* 12 (6): 1751–79. https://doi.org/10.1039/c9ee00206e.

Long, Jiang, Hu Song, Xiang Jun, Su Sheng, Sun Lun-Shi, Xu Kai, and Yao Yao. 2012. “Release Characteristics of Alkali and Alkaline Earth Metallic Species during Biomass Pyrolysis and Steam Gasification Process.” *Bioresource Technology* 116: 278–84. https://doi.org/10.1016/j.biortech.2012.03.051.

Loo, Sjaak Van, and Jaap Koppejan. 2008. *The Handbook of Biomass Combustion and Co-Firing*. London ; Sterling, VA: Earthscan. https://opac.lib.hokudai.ac.jp/opac/opac_link/bibid/2001377066 CN - Eng General Lib, Open Stacks (Foreign Books) 662.88/V26 (hardback).

Lv, Dangzhen, Minghou Xu, Xiaowei Liu, Zhonghua Zhan, Zhiyuan Li, and Hong Yao. 2010. "Effect of Cellulose, Lignin, Alkali and Alkaline Earth Metallic Species on Biomass Pyrolysis and Gasification." *Fuel Processing Technology* 91 (8): 903–9. https://doi.org/10.1016/j.fuproc.2009.09.014.

Ma, Zhongqing, Dengyu Chen, Jie Gu, Binfu Bao, and Qisheng Zhang. 2015. "Determination of Pyrolysis Characteristics and Kinetics of Palm Kernel Shell Using TGA-FTIR and Model-Free Integral Methods." *Energy Conversion and Management* 89: 251–59. https://doi.org/10.1016/j.enconman.2014.09.074.

Maxwell, D., B. A. Gudka, J. M. Jones, and A. Williams. 2020. "Emissions from the Combustion of Torrefied and Raw Biomass Fuels in a Domestic Heating Stove." *Fuel Processing Technology* 199 (October 2019): 106266. https://doi.org/10.1016/j.fuproc.2019.106266.

McKendry, Peter. 2002. "Energy Production from Biomass (Part 1): Overview of Biomass." *Bioresource Technology* 83 (1): 37–46. https://doi.org/10.1016/S0960-8524(01)00118-3.

Meca, Departmento De Engenharia. 1999. "Stages in the Burning of Coal Particles" 579: 567–79.

Míguez, José Luis, Jacobo Porteiro, Frank Behrendt, Diana Blanco, David Patiño, and Alba Dieguez-Alonso. 2021. "Review of the Use of Additives to Mitigate Operational Problems Associated with the Combustion of Biomass with High Content in Ash-Forming Species." *Renewable and Sustainable Energy Reviews* 141 (February). https://doi.org/10.1016/j.rser.2020.110502.

Mlonka-Mędrala, Agata, Aneta Magdziarz, Marcin Gajek, Katarzyna Nowińska, and Wojciech Nowak. 2020. "Alkali Metals Association in Biomass and Their Impact on Ash Melting Behaviour." *Fuel* 261 (February): 116421. https://doi.org/10.1016/j.fuel.2019.116421.

Morakinyo, Oyewale, Matlou Mokgobu, Murembiwa Mukhola, and Raymond Hunter. 2016. "Health Outcomes of Exposure to Biological and Chemical Components of Inhalable and Respirable Particulate Matter." *International Journal of Environmental Research and Public Health* 13 (6): 592. https://doi.org/10.3390/ijerph13060592.

Nakayama, Tomoki, Yutaka Matsumi, and Keiko Kawahito & Yoshifumi Watabe. 2018. "Development and Evaluation of a Palm-Sized Optical PM 2.5 Sensor." *Aerosol Science and Technology* 52 (1): 2–12. https://doi.org/10.1080/02786826.2017.1375078.

Niu, Yanqing, Houzhang Tan, and Shi'En Hui. 2016. "Ash-Related Issues during Biomass Combustion: Alkali-Induced Slagging, Silicate Melt-Induced Slagging

(Ash Fusion), Agglomeration, Corrosion, Ash Utilization, and Related Countermeasures." *Progress in Energy and Combustion Science*. Elsevier Ltd. https://doi.org/10.1016/j.pecs.2015.09.003.

Nunes, Leonel J. R. 2020. "Torrefied Biomass as an Alternative in Coal-Fueled Power Plants: A Case Study on Grindability of Agroforestry Waste Forms." *Clean Technologies* 2 (3): 270–89. https://doi.org/10.3390/cleantechnol2030018.

Ok, Yŏng-sik, Daniel C W Tsang, Nanthi Bolan, and Jeffrey Novak. 2019. *Biochar from Biomass and Waste : Fundamentals and Applications*. Amsterdam: Elsevier. https://opac.lib.hokudai.ac.jp/opac/opac_link/bibid/2001773988 CN - Agriculture, Library 662.88/OK1.

Raman, P., J. Murali, D. Sakthivadivel, and V. S. Vigneswaran. 2013. "Performance Evaluation of Three Types of Forced Draft Cook Stoves Using Fuel Wood and Coconut Shell." *Biomass and Bioenergy* 49: 333–40. https://doi.org/10.1016/j.biombioe.2012.12.028.

Rebbling, Anders, Peter Sundberg, Jonathan Fagerström, Markus Carlborg, Claes Tullin, Dan Boström, Marcus Öhman, Christoffer Boman, and Nils Skoglund. 2020. "Demonstrating Fuel Design to Reduce Particulate Emissions and Control Slagging in Industrial-Scale Grate Combustion of Woody Biomass." *Energy and Fuels* 34 (2): 2574–83. https://doi.org/10.1021/acs.energyfuels.9b03935.

Riaza, Juan, Patrick Mason, Jenny M. Jones, Jon Gibbins, and Hannah Chalmers. 2019. "High Temperature Volatile Yield and Nitrogen Partitioning during Pyrolysis of Coal and Biomass Fuels." *Fuel* 248 (December 2018): 215–20. https://doi.org/10.1016/j.fuel.2019.03.075.

Shen, Huizhong, Zhihan Luo, Rui Xiong, Xinlei Liu, Lu Zhang, Yaojie Li, Wei Du, et al. 2021. "A Critical Review of Pollutant Emission Factors from Fuel Combustion in Home Stoves." *Environment International* 157: 106841. https://doi.org/10.1016/j.envint.2021.106841.

Słupianek, Aleksandra, Alicja Dolzblasz, and Katarzyna Sokołowska. 2021. "Xylem Parenchyma—Role and Relevance in Wood Functioning in Trees." *Plants* 10 (6). https://doi.org/10.3390/plants10061247.

Spokas, K. A., J. M. Novak, C. A. Masiello, M. G. Johnson, E. C. Colosky, J. A. Ippolito, and C. Trigo. 2014. "Physical Disintegration of Biochar: An Overlooked Process." *Environmental Science and Technology Letters* 1 (8): 326–32. https://doi.org/10.1021/ez500199t.

Sun, Jian, Zhenxing Shen, Yue Zhang, Qian Zhang, Furong Wang, Tao Wang, Xiaojian Chang, et al. 2019. "Effects of Biomass Briquetting and Carbonization on PM2.5 Emission from Residential Burning in Guanzhong Plain, China." *Fuel* 244 (November 2018): 379–87. https://doi.org/10.1016/j.fuel.2019.02.031.

Tarín-Carrasco, Patricia, Ulas Im, Camilla Geels, Laura Palacios-Peña, and Pedro Jiménez-Guerrero. 2021. "Contribution of Fine Particulate Matter to Present and Future Premature Mortality over Europe: A Non-Linear Response." *Environment*

International 153 (March). https://doi.org/10.1016/j.envint.2021.106517.

Valmari, Tuomas, Esko I. Kauppinen, Juha Kurkela, Jorma K. Jokiniemi, George Sfiris, and Hannu Revitzer. 1998. "Fly Ash Formation and Deposition during Fluidized Bed Combustion of Willow." *Journal of Aerosol Science* 29 (4): 445–59. https://doi.org/10.1016/S0021-8502(97)10021-0.

Vassilev, Stanislav V., David Baxter, Lars K. Andersen, and Christina G. Vassileva. 2010. "An Overview of the Chemical Composition of Biomass." *Fuel* 89 (5): 913–33. https://doi.org/10.1016/j.fuel.2009.10.022.

Vassilev, Stanislav V., Christina G. Vassileva, Yun Cai Song, Wen Ying Li, and Jie Feng. 2017. "Ash Contents and Ash-Forming Elements of Biomass and Their Significance for Solid Biofuel Combustion." *Fuel* 208: 377–409. https://doi.org/10.1016/j.fuel.2017.07.036.

Wang, Wenyu, Chang Wen, Changkang Li, Meng Wang, Xiaomin Li, Ying Zhou, and Xun Gong. 2019. "Emission Reduction of Particulate Matter from the Combustion of Biochar via Thermal Pre-Treatment of Torrefaction, Slow Pyrolysis or Hydrothermal Carbonisation and Its Co-Combustion with Pulverized Coal." *Fuel* 240 (December 2018): 278–88. https://doi.org/10.1016/j.fuel.2018.11.117.

Wang, Yang, Dongxu Wang, Changqing Dong, and Yongping Yang. 2017. "The Behaviour and Reactions of Sodium Containing Minerals in Ash Melting Process." *Journal of the Energy Institute* 90 (2): 167–73. https://doi.org/10.1016/j.joei.2016.02.007.

Weber, Kathrin, and Peter Quicker. 2018. "Properties of Biochar." *Fuel* 217 (December 2017): 240–61. https://doi.org/10.1016/j.fuel.2017.12.054.

WHO. 2021. "WHO Global Air Quality Guidelines." *Coastal And Estuarine Processes*, 1–360.

Williams, A., J. M. Jones, L. Ma, and M. Pourkashanian. 2012. "Pollutants from the Combustion of Solid Biomass Fuels." *Progress in Energy and Combustion Science* 38 (2): 113–37. https://doi.org/10.1016/j.pecs.2011.10.001.

World Health Organization. 2021. "Setting National Voluntary Performance Targets for Cookstoves."

Yang, Haiping, Rong Yan, Hanping Chen, Dong Ho Lee, and Chuguang Zheng. 2007. "Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis." *Fuel* 86 (12–13): 1781–88. https://doi.org/10.1016/j.fuel.2006.12.013.

Yang, Wei, Youjian Zhu, Wei Cheng, Huiying Sang, Haiping Yang, and Hanping Chen. 2017. "Characteristics of Particulate Matter Emitted from Agricultural Biomass Combustion." https://doi.org/10.1021/acs.energyfuels.7b00229.

Yang, Wu, Deepak Pudasainee, Rajender Gupta, Wei Li, Zijian Song, Ben Wang, and Lushi Sun. 2020. "Particulate Emission from Municipal Solid Waste Combustion : Effect of Si−Al-Based Additives for Its Mitigation." https://doi.org/10.1021/acs.energyfuels.0c02183.

Yang, Wu, Deepak Pudasainee, Rajender Gupta, Wei Li, Ben Wang, and Lushi Sun. 2020. *An Overview of Inorganic Particulate Matter Emission from Coal/Biomass/MSW Combustion: Sampling and Measurement, Formation, Distribution, Inorganic Composition and Influencing Factors*. *Fuel Processing Technology*. Vol. 213. Elsevier B.V. https://doi.org/10.1016/j.fuproc.2020.106657.

Yao, Xiwen, Kaili Xu, and Yu Liang. 2016. "Comparing the Thermo-Physical Properties of Rice Husk and Rice Straw as Feedstock for Thermochemical Conversion and Characterization of Their Waste Ashes from Combustion." *BioResources* 11 (4): 10549–64. https://doi.org/10.15376/BIORES.11.4.10549-10564.

Yogalakshmi K N, Poornima Devi T, Sivashanmugam P, Kavitha S, Yukesh Kannah R, Sunita Varjani, S. AdishKumar, Gopalakrishnan Kumar, and Rajesh Banu J. 2022. "Lignocellulosic Biomass-Based Pyrolysis: A Comprehensive Review." *Chemosphere* 286 (P2): 131824. https://doi.org/10.1016/j.chemosphere.2021.131824.

Zhang, Qi, Jie Chang, Tiejun Wang, and Ying Xu. 2007. "Review of Biomass Pyrolysis Oil Properties and Upgrading Research." *Energy Conversion and Management* 48 (1): 87–92. https://doi.org/10.1016/j.enconman.2006.05.010.

Zhu, Xiefei, Claudia Labianca, Mingjing He, Zejun Luo, Chunfei Wu, Siming You, and Daniel C.W. Tsang. 2022. "Life-Cycle Assessment of Pyrolysis Processes for Sustainable Production of Biochar from Agro-Residues." *Bioresource Technology* 360 (June): 127601. https://doi.org/10.1016/j.biortech.2022.127601.

Zhu, Youjian, Wei Yang, Jiyuan Fan, Tao Kan, Wennan Zhang, Heng Liu, Wei Cheng, Haiping Yang, Xuehong Wu, and Hanping Chen. 2018. "Effect of Sodium Carboxymethyl Cellulose Addition on Particulate Matter Emissions during Biomass Pellet Combustion." *Applied Energy* 230 (November): 925–34. https://doi.org/10.1016/j.apenergy.2018.09.013.

APPENDIX

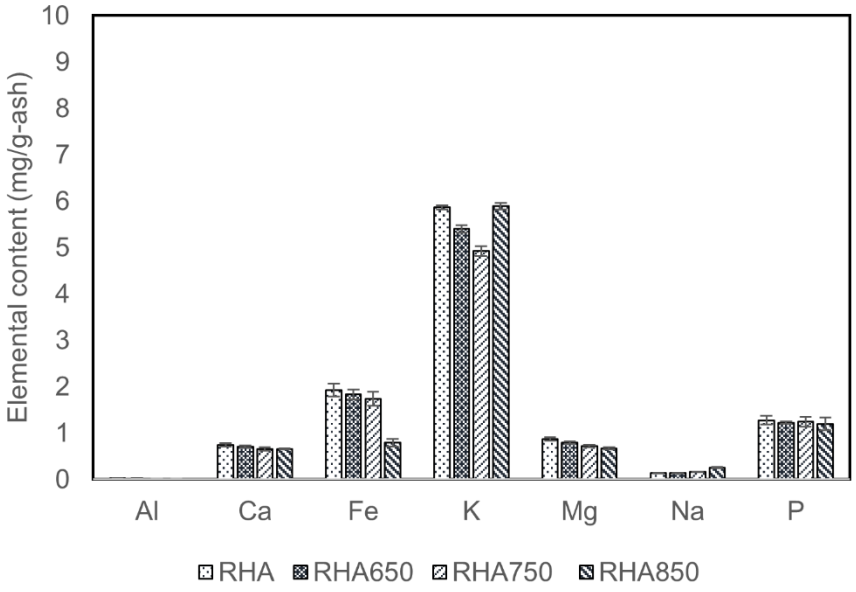


Fig. S1 Rice husk (RH) ash mineral content

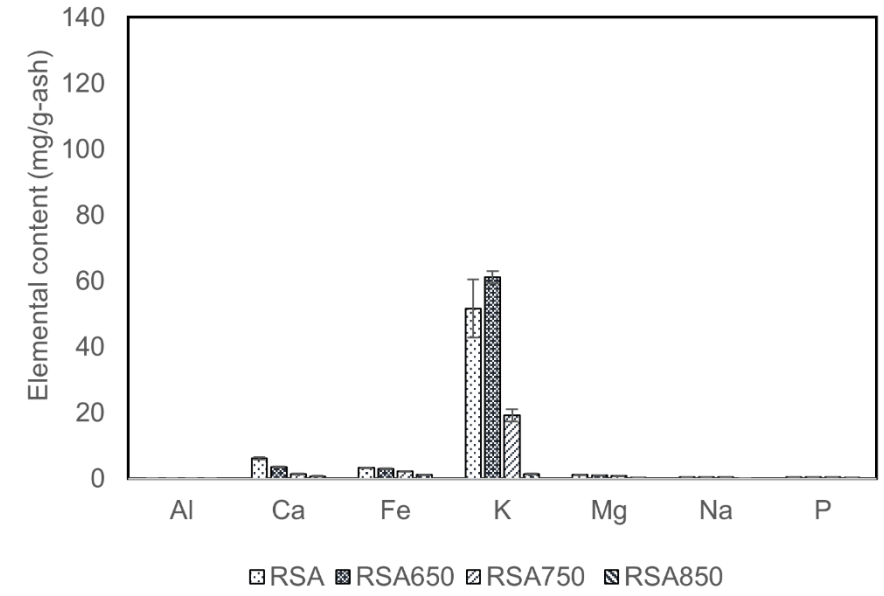


Fig. S2 Rice straw (RS) ash mineral content

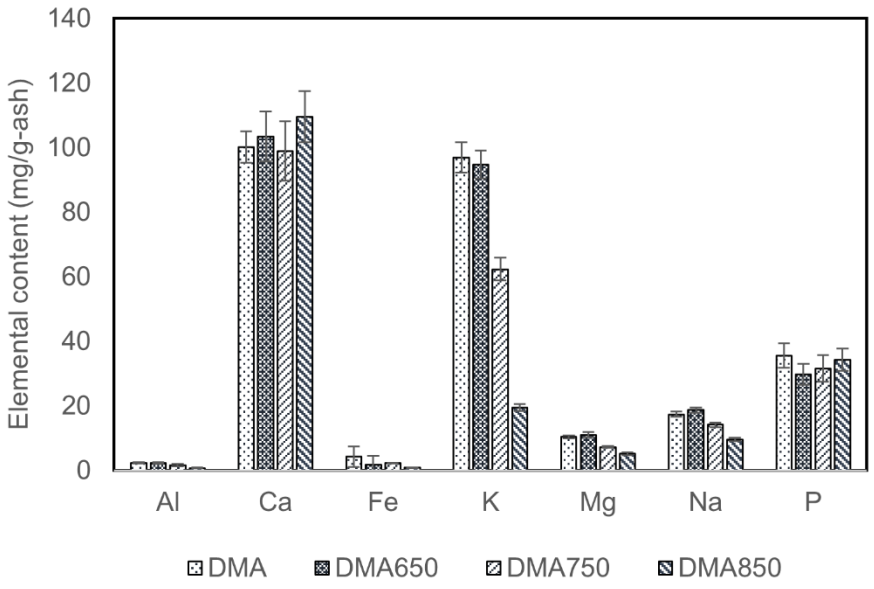


Fig.S3 Dairy manure (DM) ash mineral content