Influence of Relative Humidity and Aging on Morphology and Chemical Composition on Biomass Burning Particle

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ABSTRACT

Agricultural waste burning is a major source of fine particulate matter (FPM), which remains in long-term suspension in the atmosphere during the aging processes. This research studied changes in the size, morphology, and chemical composition of FPM produced from rice straw and sugarcane leaf burning and the effects of relative humidity (RH) on the aging process. The FPM was measured using a scanning mobility particle sizer and the particle mass was collected for morphological (transmission electron microscopy) and chemical (organic and elemental carbon, and water-soluble ions) analyses during 3, 6, and 9 h of aging. The geometric mean diameter (GMDN) of FPM from biomass burning were 95 ± 4 nm (Aitken mode) and 133 ± 40 nm (accumulation mode). The FPM changed from non-uniform and aggregate shapes in fresh particles into chain aggregates in 9 h-aged particles. The dominant chemical components of FPM were OC2, OC3, NO3–, Na+, and K+ under low RH condition (60%). Under high RH condition (90%), the FPM had a larger GMDN and a significant influence on its morphology, as observed in coated spherical or agglomerated shapes. The results showed that the aging process, RH, and aging duration were important factors affecting the size, shape, and chemical composition of aged particles.

Keywords: Aging process, Fine particulate matter (FPM), Rice straw, Size distribution, Sugarcane leaves

1 INTRODUCTION

In Thailand, air pollution has been prevalent from particulate matter from biomass burning especially particles less than 2.5 μm in diameter that are generally referred to as fine particulate matter (FPM). FPM emission control is a national and global challenge owing to the long-term suspension of fine particles in the air and their impact on human health and global climate (Guo et al., 2014; Kwon et al., 2020; Breitner-Busch et al., 2023). Previous studies reported that FPM from biomass burning in Chiang Rai and Bangkok comprised 35–40% of the total PM2.5 during the haze period (Kayee et al., 2020) and 41–46% of the biomass burning in Bangkok, Samut Prakan, and Samut Sakhon (Chuersuwan et al., 2008; Amphalop et al., 2023). Thailand is the 6th and 5th largest producer of rice and sugarcane worldwide, respectively (FAO, 2021). The main biomass of crop residue burning comes from rice straw and sugarcane, which showed 86% of its total burnt residue. Crop residues of rice and pre-harvest sugarcane have been burned, averaging approximately...
that fresh atmospheric particles are coated with water vapor and inorganic compounds (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) (Bougiatioti et al., 2015; Gong et al., 2012; Guo et al., 2014; Zimmerman et al., 2020). PM can be divided into three modes: nuclei (Dp: < 20 nm), Aitken (Dp: 20–100 nm), and accumulation (Dp: 100–1000 nm) (Shi et al., 2007; Zhang et al., 2016; Zhou et al., 2020).

In the aging process, fresh particles are emitted from direct sources, and the condensation of hot vapor occurs in the nuclei mode. After condensation and coagulation, fresh particles gradually form aggregates and chains in the Aitken mode and grow into larger particles in the accumulation mode, with homogeneous chemical processes related to the RH (Shi et al., 2007; Hennigan et al., 2012; Li et al., 2015; Zhang et al., 2016; Davies and Wilson, 2018; Zhou et al., 2020; Song et al., 2021). In addition, condensation nuclei can be coated on the surface by condensed low-volatility vapor and coagulated by heterogeneous chemical processes, particularly under high RH condition (85–95% RH) (Li et al., 2015; Davies and Wilson, 2018). In addition, the particle aging process can change its atmospheric particle number concentration and size distribution (Khalizov et al., 2009; Lewis et al., 2009; Kulmala et al., 2010; Rubasinghege and Grassian, 2013).

Typically, the geometric mean diameter (GMD$_{D_0}$) of fresh biomass particles (FBP) is in the range 100–200 nm (Li et al., 2015; Gong et al., 2016). Particles grow via condensation and coagulation during aging (Guo et al., 2014). Previous studies on biomass burning particles have shown a wide variation in particle size distribution owing to different types of crop residues and combustion conditions. Rice residues particles had a unimodal size distribution with a peak size of 62 nm, whereas corn residue particles showed a bimodal size distribution with a narrower peak at 53 nm and a larger, broader peak at 126 nm (Ma et al., 2019).

The influence of the aging process on the chemical composition of biomass burning particles has direct and indirect effects on the microclimatology, such as organic carbon (OC), elemental carbon (EC), and water-soluble ions (WSI). However, few studies have been conducted on the chemical composition changes of aged particles in ambient and laboratory chambers during 1–4 h-aging time (Zhang et al., 2011; Li et al., 2015; Song et al., 2021). Previous studies have reported that fresh atmospheric particles are coated with water vapor and inorganic compounds (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) (Bougiatioti et al., 2014; Wittbom et al., 2014; Wu et al., 2017). In addition, the dominant chemical components of fresh rice straw particles are K$^+$, Na$^+$, Cl$^-$, and SO$_4^{2-}$ (Ma et al., 2019; Seo et al., 2020; Song et al., 2021; Rattanapotanan et al., 2023).

The enhancement ratios of organic and inorganic compounds in aged crop residue particles were higher than those in fresh particles because of the production of secondary inorganic and organic compounds during aging. The RH has been attributed to changes in particle size, distribution, and chemical composition (Li et al., 2015). Meteorological data at the Air Pollutants Monitoring Tower, Kasetsart University, Bangkok showed the maximum of high RH in rainy season (May–Oct) and low RH in winter season (Nov–Feb). Aging particles under high RH condition can grow to the accumulation mode, having irregular shapes and collapsed aggregates with dominant inorganic compounds of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$. Therefore, an experiment is required on the aging process.

Rice straw (C3 plant) and sugarcane leaves (C4 plant) are primarily composed of three polymers: cellulose, hemicellulose, and lignin, with rice straw being composed of 29–34% cellulose, 23–26% hemicellulose, and 14–19% lignin (Isikgor and Becer, 2015; Passoth and Sandgren, 2019; Morya et al., 2023), while sugarcane leaves being composed of 28–50% cellulose, 19–35% hemicellulose, and 15–20% lignin (Moodley and Kana, 2015; Patil and Deshannavar, 2017; Morya et al., 2023). Moreover, the content of plants affects their combustion. Plants with a high cellulose content have a faster combustion rate and plants with a high hemicellulose content exhibit high thermal decomposition (Gani and Naruse, 2007; Wang et al., 2008; Wang et al., 2020).

FPM pollution from biomass burning is a severe environmental problem that affects human health and global climate (Li et al., 2007; Lin et al., 2010; Cao et al., 2011; Zhang et al., 2011; Wu et al., 2017). Previous studies have suggested that biomass burning is an important source of cloud condensation nuclei (CCN). Biomass particles affect atmospheric particle characteristics, such as hygroscopicity and cloud-nucleating ability, which increase significantly with photooxidation (Engelhart et al., 2012; Ma et al., 2019; Pariyothon et al., 2023). FPM remains suspended in the atmosphere for days to weeks and is dispersed over long distances as a result of complex physical and chemical reactions between fresh particles and gases called aged particles (Cheung et al., 2011; Guo et al., 2014; Zimmerman et al., 2020). PM can be divided into three modes: nuclei (Dp: < 20 nm), Aitken (Dp: 20–100 nm), and accumulation (Dp: 100–1000 nm) (Shi et al., 2007; Zhang et al., 2016; Zhou et al., 2020).

6.2 and 0.9 million t, respectively, in 2021, resulting in fine particle pollution in the atmosphere (FAO, 2021).

Rice straw (C3 plant) and sugarcane leaves (C4 plant) are primarily composed of three polymers: cellulose, hemicellulose, and lignin, with rice straw being composed of 29–34% cellulose, 23–26% hemicellulose, and 14–19% lignin (Isikgor and Becer, 2015; Passoth and Sandgren, 2019; Morya et al., 2023), while sugarcane leaves being composed of 28–50% cellulose, 19–35% hemicellulose, and 15–20% lignin (Moodley and Kana, 2015; Patil and Deshannavar, 2017; Morya et al., 2023). Moreover, the content of plants affects their combustion. Plants with a high cellulose content have a faster combustion rate and plants with a high hemicellulose content exhibit high thermal decomposition (Gani and Naruse, 2007; Wang et al., 2008; Wang et al., 2020).
of particles over 4 h both of low and high RH condition. Furthermore, there is lack of information of sugarcane leaves and rice straw using similar experimental condition. Consequently, this study aims to investigate the changes in the size distribution, morphology, and chemical composition of fresh and aged particles produced resulting from rice straw and sugarcane leaf burning under low and high relative humidity conditions in a laboratory chamber. The contributions of the particle size, carbon, and WSI compositions of the particles and the influence of RH on the aging processes are discussed. The results are beneficial for a better understanding of the biomass aging process and will lead to the management of FPM problems during biomass burning activities to reduce their impact on air pollution and climate change.

2 MATERIALS AND METHODS

2.1 Experimental Setup

All samples of rice straw and sugarcane leaves were collected during the same planting season in agricultural areas in Thailand. The rice straw and sugarcane leaves were cut into 1 cm length and dried at 90°C for 1 h in an oven. The dried samples were stored in a desiccator and cooled to room temperature. Fig. 1 shows the experimental setup, which comprised a 30×30×60 cm biomass burning chamber, a 60 × 60 × 80 cm mixing chamber, a humidifier and the following equipment: humidity meter and temperature transmitter (Humidity/Temperature transmitter, EE Elektronik, Model EE33, Engerwitzdorf, Austria), Humidifier (Ultrasonic Humidifier, Anhui Jingng industrial, Model JGA-102, China), vacuum pump, personal DataRAM (pDR1500, Thermo Scientific, Waltham, USA), scanning mobility particle sizer (SMPS) with electrostatic classifier (Electrostatic classifier, TSI, Model 3080, Shoreview, USA), advance aerosol neutralizer (Aerosol neutralizer TSI, Model 3087, Shoreview, USA), differential mobility analyzer (DMA, TSI, Model 3081, Shoreview, USA), and nano water-based condensation particle counter (N-WCPC, TSI, Model 3788, Shoreview, USA).

Before each biomass burning experiment, the burning and mixing chambers were cleaned with HEPA-filtered air using a 27.3 L min⁻¹ vacuum pump for 30 min. Fresh air was exchanged that was equal to approximately 3 times the volume of the mixing chamber. The air between the biomass burning and mixing chambers was opened, allowing biomass particles and gases to enter the mixing chamber with a 27.3 L min⁻¹ vacuum pump. The humidity and temperature transmitter was located at the top of the mixing chamber and 30 cm from the humidifier. To control the

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**Fig. 1.** Experimental setup with (1) HEPA filter, (2) Biomass burning chamber, (3) Mixing chamber, (4) Fan, (5) Humidifier, (6) Humidity and temperature transmitter, (7) Pump, (8) pDR1500, (9) Electrostatic classifier, and (10) N-WCPC.
relative humidity, the humidifier with ultrapure water was used to increase the relative humidity in the air and controlled by a valve before feeding to the chamber. The dried samples (0.5 g) were completely burned in the biomass burning chamber with HEPA-filtered air. The pDR-1500 was located after the mixing chamber to investigate the initial mass concentration of biomass burning particles and to collect FPM for physical and chemical analyses. The FPM mass concentration was measured using the pDR-1500 until 900 µg m⁻³ ± 5%, after which the valve was turned off. In the mixing chamber, the biomass particles were mixed simultaneously using two mixing fans, each with a diameter of 12 cm and operating at 2,550 rpm. The RH and temperature in the mixing chamber were 60 ± 5% and 33.4–33.8°C, as measured by the humidity and temperature transmitter throughout the 9-hour experiment. The biomass burning particles were investigated in terms of their number, concentration, morphology, and chemical composition. All experiments of rice straw and sugarcane leaves burning were repeated 3 times.

2.2 FPM Measurement and Sampling
The FPM was measured and sampled based on aging durations of 3, 6, and 9 h. The FPM that passed the advance aerosol neutralizer was size classified using an electrostatic classifier coupled with the DMA with a scanning mode of 64 channels. The scan size range was 16.8–791.5 nm. The monodisperse particles from the DMA were split using a sheath flow rate of 2.4 L min⁻¹ and entered into the N-WCPC. The FPM number concentrations were counted using the N-WCPC with a sample flow rate of 0.6 L min⁻¹. At the beginning of each sampling hour, the number concentration was measured for 8 cycles (135 sec cycle⁻¹) with a total scanning time of 18 min.

The FPM was collected on 37 mm diameter quartz fiber filters (TE-QMA-37, Tisch Environmental Inc., OH, USA). The filters were heated at 550°C for 1 h before sampling to remove carbonaceous contaminants (Phairuang et al., 2021; Choomanee et al., 2024) and then cooled to ambient temperature before placement in the pDR1500 at a 1.52 L min⁻¹ flow rate. The samples were collected for 30 min at 2.5–3 h, 5.5–6 h, and 8.5–9 h to represent the aged particles at 3, 6, and 9 h, respectively. The samples were kept at 4°C before the investigation of their shape and chemical composition.

2.3 Morphological Analysis
The FPM samples were cut and extracted in ultrapure water using ultrasonic cleaner for 60 min. The samples were dropped onto 300-mesh copper grids coated with a Formvar film (Marvanová et al., 2018). The morphologies of the sample were analyzed using a transmission electron microscope (TEM; Hitachi, Model HT7700, Ibaraki, Japan) operating at an accelerating voltage of 120 kV. Therefore, all grid areas were investigated as particle spots. The diameter and shape of the biomass burning particles were analyzed using ImageJ software (version 1.53 J National Institutes of Health, USA).

2.4 Chemical Analysis
The chemical characteristics of the FPM samples were analyzed for carbon components and WSI. A carbon analyzer (Sunset Laboratory, Model 4 L Methanator/Detector assembly, OR, USA) was used to quantify the carbon concentration using the IMPROVE thermal/optical reflectance protocol (Phairuang et al., 2022). The samples were punched into 1.5 cm², placed on a sample port, and analyzed in two phases. In phase 1, the samples were heated with pure helium oxidizing gas to quantify the OC. The differential volatilization temperatures of OC1, OC2, OC3, and OC4 were 120, 250, 450, and 550°C, respectively. As the evolved carbon flows through a manganese oxide (MnO₂) oven, it was converted to carbon dioxide (CO₂) gas, which was carried in a helium (He) stream. The flow of helium containing the carbon dioxide passed to a methanator oven where the CO₂ was reduced to methane. The methane was detected using a flame ionization detector system (Birch and Cary, 1996). The split point between these phases was automatically set when the measured optical signal returns to the baseline to minimize uncertainty due to pyrolytic carbon (PC) formation from the OC into a thermally stable form, which was similar to EC (Bautista et al., 2015). In phase 2, an oxidizing carrier gas (He with 2% oxygen) was introduced at 580°C to quantify EC. The volatilization of EC1, EC2, and EC3 occurred at 550, 700, and 800 °C, respectively,
in which EC was detected. The limits of detection of OC and EC were 0.2 and 0.40 µg cm⁻², respectively. Total OC and EC were defined as follows: OC = OC1 + OC2 + OC3 + OC4 + PC and EC = EC1 + EC2 + EC3 – PC (Gu et al., 2010). The OC and EC analyses were calibrated prior to use based on a series of 3.68 µC mL⁻¹ sucrose solutions (Sunset Laboratory Inc.) (N = 5, R² = 0.99).

All samples were determined for nine ions: sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), lithium (Li⁺), ammonium (NH₄⁺), chloride (Cl⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻). The remaining 2.55 cm² samples were extracted with 10 mL ultrapure water using an ultrasonic cleaner (Powersonic410, Hwashin Technology Company, Korea) for 60 min and passed through 0.45 µm nylon syringe filters (Filter-Bio). The samples were analyzed using ion chromatography (Ion chromatograph system, Model. Dionex ICS-1100, Thermo Scientific, Waltham, USA) with a cation column (Cation column, Model. Dionex IonPac™ CS12A RFIC™, Thermo Scientific, Waltham, USA) and an anion column (Anion column, Model. Dionex IonPac™ AS22 RFIC™, Thermo Scientific, Waltham, USA). The limit of detection for both the anion and cation was 0.001 µg mL⁻¹. The ion chromatograph was calibrated prior to use using a standard with six cations and three anions (Thermo Scientific) (N = 5, R² = 0.99).

2.5 Effect of High RH on Selected Biomass-aged Particles

Selected biomass was cut into 1 cm and dried at 90°C for 1 h in an oven. The dried samples were completely burned in a biomass burning chamber. The FBP and soot were sucked into the mixing chamber with a 27.3 L min⁻¹ flow pump vacuum pump for 10 s. Subsequently, the valve was turned off. In the mixing chamber, FPM was mixed with air using a fan. The RH was continuously maintained at 90 ± 5% using a humidifier with ultrapure water. The temperature in the mixing chamber was 31.1–31.8°C measured using the humidity and temperature transmitter throughout the 9-h experiment. The size distribution was classified using the electrostatic classifier coupled with the DMA and entered the N-WCPC. The samples were collected on a quartz fiber filter with a diameter of 37 mm using the pDR1500 at 1.52 L min⁻¹ for aging times of 3, 6, and 9 h to investigate the shape and to analyze the chemical composition, including carbon components and WSI.

3 RESULTS AND DISCUSSION

3.1 Size Distribution Variation of Fresh and Aged Particles

Fig. 2 shows the variation of the average FPM number concentrations of rice straw and sugarcane leaves from 0 to 9 h. The measurement of the number concentration included 8 cycles h⁻¹ with a scanning time of 18 min. The FBP emitted from rice straw at 60% RH was characterized as dominant by unimodal distribution. The initial peak particle diameter was between 59.4 and 151.2 nm with a number concentration of 1.08 × 10⁵ to 2.17 × 10⁶ particle cm⁻³ (Fig. 2(a)), which was in line with previous studies (Zhang et al., 2011; Seo et al., 2020). At 3 and 9 h aging times, the particle number concentrations of 59.4 and 151.2 nm decreased to 1.44 × 10⁴ to 5.22 × 10⁴ particle cm⁻³ and 4.53 × 10³ to 8.48 × 10⁴ particle cm⁻³, respectively. Rice straw burning released the highest particle number concentration at 0 to 1 h, then the FPM continuously decreased until 9 h. Fig. 2(b) shows that the FBP emitted from sugarcane leaves at 60% RH was dominant by unimodal distribution, with the initial peak particle diameter between 66.1 and 310.6 nm with a number concentration of 8.88 × 10⁴ to 2.03 × 10⁵ particle cm⁻³. The FBP of the open burning of sugarcane leaves had a particle diameter peak similar to that in a previous biomass burning study (Dattamudi et al., 2020). At 3 and 8 h aging times, the particle number concentrations of 66.1 and 151.2 nm were 1.44 × 10⁴ to 5.22 × 10⁴ particle cm⁻³ and 4.53 × 10³ to 8.48 × 10⁴ particle cm⁻³, respectively. Rice straw burning released the highest particle number concentration at 0 to 1 h, then the FPM continuously decreased until 9 h. The FPM from rice straw burning at 60% RH had a slightly higher number concentration than that of sugarcane leaf burning. Rice straw, a C3 crop, emits more FPM number concentrations and carbon monoxide (CO), methane (CH₄), and non-methane hydrocarbons than sugarcane leaves (C4 crop) (Vernooij et al., 2022). The number concentration
increased from 2 h to 8 h, which could be attributed to coagulation, the dry deposition process, wall losses, turbulent coagulation, and dilution due to the sampling. The dilution in the mixing chamber effects on the rate of Brownian agglomeration (Park et al., 2002; Zhang et al., 2011; Shou et al., 2019).

Fig. 3 shows the time series of the FPM GMDN resulting from rice straw and sugarcane leaf burning in the chamber at 60% RH. The rice straw FPM changed from fresh to aged particles within 0 to 4 h, with its GMDN increasing from 95 ± 4 to 106 ± 11 nm. The GMDN decreased at 5 h to 97 ± 23 nm and gradually decreased until the 9 h to 90 ± 25 nm. The GMDN of FPM from rice straw burning was mainly in the Aitken mode at 90–106 nm, which is consistent with the results of a previous study (Li et al., 2015). Meanwhile, sugarcane leaves FPM changed from fresh to aged particles within 0 to 2 h, with the GMDN of FPM from sugarcane leaf burning increasing from 133 ± 40 to 152 ± 39 nm. The released particles were large and the GMDN was in the accumulation mode range. Particles in accumulation mode are most susceptible to chemical transformation by heterogeneous, condensation, and coagulation processes (Davies and Wilson, 2018). Therefore, the GMDN of sugarcane leaves FPM increased rapidly at 1 – 2 h and then continued to decrease every hour. The GMDN of sugarcane leaf particles was mainly in the Aitken and accumulation modes, with a GMDN of 80–152 nm. The GMDN in this study was consistent with those in previous studies which reported mainly ultrafine PM of 100–200 nm at 60% RH from biomass burning events and lab scale testing (Rajput et al., 2011; Zhang et al., 2015; Dattamudi et al., 2020). The geometric standard deviations of the FPM from rice straw and sugarcane leaves was 1.55–2.04 in polydisperse aerosols (Geo. Std. Dev. more than 1.25 is polydisperse) (Dechrakra et al., 2020). However, the GMDN of aged particles was varied depending on a range of relative humidity, dry weight of the biomass sample, and initial number concentration of biomass burning particles.

Fig. S1 shows the size distributions of the rice straw FPM at 60% RH are unimodal distributions (Aitken mode). The peak diameter of the fresh rice straw particles was 98.2 nm. The aging time of the rice straw particles showed the peak diameter increased from 101.8 to 113.4 nm (1–3 h) and slightly shifted by 121.9 nm after burning for 6 h. This result revealed that the peak diameter after 3–9 h increased with aging duration (Zhang et al., 2011; Seo et al., 2020). The size distributions of sugarcane leaves FPM at 60% RH are unimodal distributions (accumulation mode). The peak diameter of the fresh sugarcane leaf particles was 140.7 nm, which was larger than that of rice straw. After 1 h of aging, the peak diameter of sugarcane leaf burning increased to 168.5 nm, which was increased more clearly than that of rice straw. After 2–8 h, the peak diameter did not change with aging time. However, it should be noted that the 9 h aging time showed a peak diameter of 71 nm. The smaller peak diameter for the longer aging duration resulted from the
gas-to-particle reaction process, causing new particle formation in the Aitken mode and growth by the condensation of low-volatility gases onto the particles (Zhang et al., 2011; Li et al., 2017). The evolution of the size distribution can be explained by the aging time and biomass type. These results showed that the number concentration, GMDN and peak diameter of the FPM from both biomass types changed from 0 to 3 h. Therefore, the study of particle shape and chemical composition was divided into three sampling periods: 0–3, 4–6, and 7–9 h of aging.

3.2 Evolution of FPM Shape with Aging Duration

Fig. 4 shows the shapes of the fresh and aged emitted by biomass burning, which were investigated using TEM. The FPM evolution, 0–3 h after rice straw burning, emitted ultrafine PM with a non-uniform and aggregate shape. It occurs with particles that have only been released from biomass combustion or primary particle and condensation processes (Liu et al., 2017; Seo et al., 2020). During 4–6 h of aging, the particle was condensed and collapsed, changing to aggregates and chain aggregates. These particles were formed by condensation and coagulation processes (Reid et al., 2005). After 7 h of aging, the particles became long chains and agglomerated by coagulation and accumulation. The morphological evolution of the FPM emitted from sugarcane leaf burning from 0 to 3 h was a non-uniform and aggregate shape larger than rice straw. After 4–6 h of aging, the particle shape condensed and collapsed, changing to long chains and chain aggregates. After 7 h of aging, the particles changed to chain agglomerates, beginning the collapse of the chain and agglomerated shapes via coagulation, accumulation, and condensation. Burning sugarcane leaves releases fresh particles in the accumulation mode, which are most susceptible to chemical transformations by heterogeneous processing (Davies and Wilson, 2018). Therefore, the evolution of sugarcane leaf particles tended to change faster than that of rice straw particles. The shape changed depending on the aging duration and biomass type. Moreover, the extraction method with ultrasonic cleaner was no significant effect on the agglomeration of FPM in the size range of 170–500 nm (Marvanová et al., 2018). However, after 7 h of aging, the rice straw and sugarcane leaves also contained differently shaped particles, including irregular shapes, chain aggregates, and collapsed aggregates, which is consistent with other studies on biomass-burning fields (Torvela et al., 2014; Liu et al., 2017; Seo et al., 2020; Song et al., 2021).
3.3 Effects of Aging time on Particle Composition

The time variation of the chemical composition of biomass burning particles (OC, EC, and WSI) varied with aging time, especially the highest concentration of OC in rice straw and sugarcane leaves were 0.19–0.20 and 0.22–0.51 g kg⁻¹ dry biomass, respectively. At 9 h, the chemical composition of biomass burning particles was found higher OC concentration shown in Table S1.

The chemical components of OC and EC in the FPM emitted from burning rice straw and sugarcane leaves are listed in Table 1 and shown in Fig. S2. The OC in the rice straw and sugarcane leaf particles was the most dominant species in the total carbon composition (66–79%) for all aging times. OC2 and OC3 were the most dominant carbon species, indicating that biomass burning was the main source of combustion. The proportions of OC3 and EC1 in the rice straw particles increased slightly with aging. The carbon composition of the sugarcane leaf particles showed that the proportion of total OC decreased with aging time. From 3 to 9 h, the chemical component trends did not change significantly. In the present study, the OC1 proportions in the sugarcane leaf particles were lower than in the rice straw particles. The results of the initial peak particle diameter and GMDn revealed that rice straw burning emitted Aitken mode particles, while sugarcane leaf burning emitted accumulation mode particles. The new particle formation from combustion in the nuclei mode particles absorbed high volatile organic matter better than particles in the accumulation mode, due to the large surface area. Owing to the smaller relative surface area in accumulation mode, less volatile organic matter could be adsorbed, leading to decreased proportions of OC1 in sugarcane leaf particles (Kittelson, 1998; Zhang et al., 2020). The average proportion of total EC in the sugarcane leaf particles was higher than that in the rice straw. Previous studies on biomass burning, which emitted accumulation mode particles, reported a higher EC content (Seo et al., 2020).

The proportions of the ionic species in the FPM from burning rice straw and sugarcane leaves are compared in Table 1 and Fig. S3. NO₃⁻ was the most dominant species for both biomass burning, followed by Na⁺, Mg²⁺, SO₄²⁻, and K⁺ for rice straw and Na⁺, K⁺, and SO₄²⁻ for sugarcane leaves. The primary chemical components found in the fresh particles generated from biomass burning were K⁺, Na⁺, and SO₄²⁻ in the FPM of the chemical fertilizers and herbicides at the agricultural site.
Table 1. Dominant species in chemical composition of biomass burning source.

<table>
<thead>
<tr>
<th>Biomass source</th>
<th>Time (h)</th>
<th>Low RH condition (60% RH)</th>
<th>High RH condition (90% RH)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>OC/EC</td>
<td>WSI</td>
</tr>
<tr>
<td>Rice straw</td>
<td>3</td>
<td>OC3, OC2, OP</td>
<td>NO3⁺, Na⁺, Mg²⁺, K⁺</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>OP, OC3, OC2</td>
<td>NO3⁺, Na⁺, Mg²⁺, K⁺</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>OP, OC3, OC2</td>
<td>NO3⁺, Na⁺, Mg²⁺, K⁺</td>
</tr>
<tr>
<td>Sugarcane leaves</td>
<td>3</td>
<td>OC3, OC4, EC1</td>
<td>Na⁺, K⁺, SO₄²⁻</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>OC3, OC2, OC4</td>
<td>NO3⁺, Na⁺, K⁺, SO₄²⁻</td>
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<tr>
<td></td>
<td>9</td>
<td>OC3, OC4, OC2</td>
<td>NO3⁺, Na⁺, K⁺</td>
</tr>
</tbody>
</table>

OC = Organic carbon; EC = Elemental carbon; WSI = Water-soluble ions.

Consequently, these three ions can serve as indicators or tracers to identify the sources of PM originating from biomass combustion fields (Li et al., 2003; Han et al., 2010; Ma et al., 2019; Seo et al., 2020; Song et al., 2021; Ratanapotanan et al., 2023). The trend of ionic species in FPM revealed that the SO₄²⁻ proportion decreases with aging duration. At 3–9 h, the Mg²⁺ content increased with aging duration. In the present study, the Na⁺ concentration trend did not change significantly. Based on documentation, Na⁺ is notably found in PM emissions originating from the smoldering combustion of rice straw fields, while SO₄²⁻ is frequently detected in FPM released during the combustion of rice straw within the combustion chamber (Hong et al., 2017; Chantara et al., 2019).

The ionic species resulting from the burning sugarcane leaves of SO₄²⁻, Na⁺, and K⁺ had proportions that decrease with aging time. From 3 to 9 h, the NO₃⁻ concentration increased with aging duration for both biomasses, showing a trend species associated with secondary aerosol production (Li et al., 2015). In contrast, the SO₄²⁻ proportion was low because of the low sulfur composition in rice straw and sugarcane leaves (Seo et al., 2020). The K⁺/OC ratios were 0.050 and 0.068 for the FPM of rice straw and sugarcane leaf burning, respectively. The K⁺/EC ratios were also determined to be 0.354 and 0.438 for the FPM of rice straw and sugarcane leaf burning, respectively (Ram and Sarin, 2010). This result showed that the K⁺/EC ratios were lower than those reported in previous studies, which could be attributed to the source of the biomass and the temperature of the burning experiment (Li et al., 2015; Ni et al., 2017; Seo et al., 2020).

The rice straw burning emitted a smaller initial peak particle diameter and smaller GMDN than sugarcane leaf burning. In Thailand in 2021, about 6 times more rice straw as a crop residue was burnt than sugarcane. Furthermore, the proportions of water-soluble ions in the chemical components from fresh and aged rice straw particles were higher than for sugarcane leaf particles. The WSI in particles under a high RH condition could affect the aging process. Therefore, rice straw was selected to investigate changes in the physical and chemical characteristics of particles at high RH condition.

### 3.4 Effect of RH on Size Distribution, Morphology, and Chemical Compositions of Rice Straw FPM

Fig. 5 shows the variation in the FPM number concentration of rice straw at 90% RH for 0 to 9 h. Fig. 5(a) shows that the FBP emitted from rice straw at 90% RH was dominated by unimodal distributions, similar to burning at 60% RH. The initial peak particle diameter under high RH condition (90% RH) between 113.4 and 187.7 nm was larger than low RH (60% RH). The initial peak number concentration of the high RH condition was 5.13 × 10⁶ to 1.40 × 10⁷ particle cm⁻³, which was 3–5 times higher than that under low RH condition. For particles aged over 3 h, rice straw particles under high RH condition indicated a rapid change in the number concentration up to 1.40 × 10⁶ particle cm⁻³ at the maximum of the initial peak particle. However, the number concentration of rice straw burning particles decreased with aging time under low RH condition. The evolution of particle size and number concentration under high RH condition must be the result of the coagulation of particles and gas-to-particle transformation processes facilitated by water vapor (Li et al., 2015). After 4 h, the number concentration tended to decrease with aging time under both low and high RH conditions.
Fig. 5(b) shows the time series of the FPM GMDN of rice straw in the chamber at 90% RH. The rice straw particle GMDN changed under high RH condition from fresh to aged particles within 0 to 3 h, from 136 to 140 nm. The GMDN tended to increase slightly until 9 h, when the aged particle size was 147 nm. The GMDN of the high RH condition was distinctly larger than that of the low RH condition throughout the duration of the experiment. Notably, in most recent studies with high RH levels exceeding 90%, the GMDN of particles also increased, indicating particle growth by heterogeneous reactions and promotion of gas-to-particle conversion (Weingartner et al., 1995; Rissler et al., 2006; Zhang et al., 2008; Lewis et al., 2009; Li et al., 2015; Davies and Wilson, 2018; Won et al., 2021).

Fig. S4 shows that rice straw FBP under both low and high RH conditions had unimodal distributions. The FBP observed at high RH was in the accumulation mode, whereas at low RH it was in the Aitken mode. The peak diameter of the fresh rice straw particles under high RH condition was 151.2 nm. Previous studies have reported that high RH can promote the growth of ultrafine PM by condensation and coagulation processes up to fine PM more than low RH conditions (Zhang et al., 2011; Li et al., 2015; Seo et al., 2020). In addition, condensation nuclei can be coated on the surface by water vapor, condensed low volatile vapor, and coagulation by heterogeneous chemical processes, especially under high RH conditions (Davies and Wilson, 2018). Even though the peak diameter of rice straw size distribution increased from 98.2 to 121.9 nm at low RH with aging time, the peak diameter at high RH was relatively stable between 145.9 and 151.2 nm with aging time (Fig. S4).

Fig 6 shows the evolution of FPM under high RH condition. This study found that 0–3 h after rice straw burning, FPM had an aggregate shape (Li et al., 2015; Liu et al., 2017; Seo et al., 2020). During 4–6 h of aging, the particle was condensed, coagulated, collapsed, and changed into larger aggregates (Reid et al., 2005). During 7–9 h of aging, the particles evolved into coated spheres or were agglomerated by coagulation. Under high RH condition, the chain-aggregate shape of the particles did not exist throughout the aging.

The chemical components of OC and EC in FPM from rice straw burning at 90% RH are shown in Table 1 and Fig. S5. The OC proportion in rice straw FPM was the most dominant species in the total carbon composition (78–85%) at all aging times. In rice straw burning under high RH condition, the OC proportion in the FPM was slightly higher than the OC proportion of low RH condition. The OC fractions were OC3, OC2, and OP, which were found to be dominant in rice straw burned at high RH. The OC2 proportion in rice straw particles at 90% RH slightly decreased with aging time.
The dominant ionic species and proportions in the FPM of rice straw burning at 90% RH are shown in Table 1 and Fig. S6, respectively. Na\(^+\) was the most dominant species in rice straw, followed by Cl\(^-\), SO\(_4^{2-}\), NH\(_4^+\), and Mg\(^{2+}\) for rice straw. The SO\(_4^{2-}\) in the rice straw FPM under the high RH condition increased with aging time due to the prominent pathway of SO\(_2\) to sulfate conversion by heterogeneous reactions or via aqueous phase oxidation within the particles (Rubasinghege and Grassian, 2013; Li et al., 2015).

4 CONCLUSION

This study provides an experimental investigation of the size distribution, morphology, and chemical composition in the aging process of particles from rice straw and sugarcane leaf biomass burning. The FBP from rice straw burning under low RH condition was in the Aitken mode, whereas sugarcane leaf particles were in the accumulation mode. The morphology of rice straw and sugarcane leaves under low RH condition evolved from non-uniform and aggregated in fresh particles to chain aggregates in 9 h-aged particles. These results confirmed that the high RH condition had a significant influence on the morphology of the particles, as demonstrated by their coated spherical or agglomerated shapes. This study revealed a larger GMD\(_N\) and peak diameter of the particles due to coagulation, growth by heterogeneous reactions, and gas-to-particle transformation processes facilitated by water vapor. Changes in the proportions of OC, EC, and ionic species in the aged particles depended on the biomass type and RH under combustion conditions. The OC\(_3\), EC\(_1\), and Mg\(^{2+}\) proportions in rice straw particles under low RH condition increased slightly with aging time. Under high RH condition, the trend of SO\(_4^{2-}\) proportion in FBPs decreased with aging time. These findings are beneficial for a better understanding of aged biomass particles and will lead to the control of FPM from agricultural waste burning, especially in environments with high RH.

LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation(s)</th>
<th>Definition(s)</th>
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<tbody>
<tr>
<td>FBP</td>
<td>fresh biomass particles</td>
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<tr>
<td>FPM</td>
<td>fine particulate matter</td>
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<tr>
<td>GMD(_N)</td>
<td>geometric mean diameter in terms of number concentration</td>
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<tr>
<td>RH</td>
<td>relative humidity</td>
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<tr>
<td>PM</td>
<td>particulate matter</td>
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<tr>
<td>OC</td>
<td>organic carbon</td>
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<td>EC</td>
<td>elemental carbon</td>
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<td>WSI</td>
<td>water-soluble ions</td>
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Fig. 6. FPM morphology from rice straw burning at 90% RH (a) at 3 h, (b) at 6 h, and (c) at 9 h.
ACKNOWLEDGMENT

This project was funded by the National Research Council of Thailand (NRCT) and the Atmospheric Science Research Group (ASRG), Faculty of Environment, Kasetsart University, Bangkok, Thailand.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.230234

REFERENCE


Zhang, T., Wooster, M.J., Green, D.C., Main, B. (2015). New field-based agricultural biomass burning trace gas, PM_{2.5}, and black carbon emission ratios and factors measured in situ at crop residue fires in Eastern China. Atmos. Environ. 121, 22–34. https://doi.org/10.1016/j.atmosenv.2015.05.010

