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Research Article

CHARACTERIZATION OF PARTICULATE MATTERS EMITTED FROM BIOMASS COMBUSTION USING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY

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ABSTRACT:
Particulate Matters (PMs) emitted from biomass combustion including open burning of biomass agricultural residues, and forest fires must be reduced to protect both human health and the environment. The physical characteristics of morphology, elemental composition and nanostructure of particulate matters generated from biomass combustion were successfully investigated by using electron microscopy and energy dispersive X-ray spectroscopy (EDS) analysis with Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), and thermogravimetric analysis (TGA) was used to analyze the oxidation kinetics of particulate matters. Before biomass burning, it was found that about 65% of carbon fraction in biomass raw material while 95% of carbon fraction in soot and 84% in ash particles after burning. The average diameter size of single primary particles is approximately 36 nm. Nanostructure of the single primary particle of biomass soot is mainly composed of curve line carbon crystallites while metallic ash nanoparticle is composed of straight-line hatch patterns. The inter-planar spacing of fringes of biomass soot and ash crystallites is 0.36 nm and 0.28 nm, respectively. This article aims to study the different nanostructure of biomass forest leaves residual ash and soot such as agglomerated particles, primary particle's measurement using TEM image analysis.

Keywords: *Biomass Combustion, Particulate Matter, Soot Nanostructure, Residual Ashes, Electron Microscopy*

1. INTRODUCTION

Particle emissions from fossil fuels combustion and biomass burning or biomass combustion are major sources of particulate matters. Emissions regulations and standards for internal combustion engines of automotive vehicles and fuels are progressively introduced on particle emissions because particulate matters are adversely affected both human health such as lung cancer, asthma and respiratory system, and environment. Thus, particle emissions standards are adopted to reduce the PMs in the global automotive industry as well. Particulate Matters (PMs) are mainly composed of volatile materials (soluble organic fraction) which are organic, sulfates, and nitrate fraction and non-volatile materials (solid fraction) such as soot and ash. Concerning with the size of atmospheric particles, it could be defined that there are PM10, D (diameter) < 10 µm; fine particles, D (diameter) < 2.5 µm; ultrafine particles, D (diameter) < 0.10 µm; and nanoparticles D (diameter) < 0.05 µm or 50nm, respectively [1-4].

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Preechar Karin et al. investigated that the average primary particle sizes of diesel and biodiesel engine's PMs are approximately 34 nm and 32 nm. The nanostructure of soot is mainly composed of curve line carbon crystallites. Nanostructures of PMs from diesel lamp and diesel engine are very similar; however, some parts of soot are agglomerated with ash contained in engine lubricant oil. The results of diesel blended with lubricating oil; metal oxide ash was found as the parallel straight-line hatch patterns. Thus, metal oxide ashes are mainly obtained from metal additives as metallic elements such as Calcium (Ca), Phosphorous (P), Sulfur (S), Magnesium (Mg), Silicon (Si) and Zinc (Zn) of engine lube oil. The diameters of the single primary of metal oxide ashes and soot particles are in the range of 10-30 nm and 10-60 nm. Thermogravimetric analysis (TGA) was used to study the oxidation kinetics of particulate matters (PMs) [5-8].

Increasing air pollution produced from various sources, including forest fires and open burning of agricultural residues which is a common practice in many Asian countries, is a major risk of public health problems and environmental impacts. Consequently, the level of PM_{10} and $PM_{2.5}$ were increased in these years. In 2005, Thailand health statistics mentioned that respiratory diseases are the rank 5th in the top ten leading causes of death with 40.10 per 100,000 populations. It was estimated that the number of global deaths is 3.7 million in 2012, and about 88% of these deaths happened in low- and middle-income (LMI) countries, which is 82% of the world population. Simone Simões Amaral et al., reviewed the particulate matter emissions from different types of biomass (open and closed) burning. The particulate emissions factor and sizes of particle emissions such as PM_1, $PM_{2.5}$, and PM_{10} were found from the burning of compacted forest biomass, agriculture, and garden biomass by laboratory, field, residences burning and combustors. [9-12].

Forest fires are one of the major sources of atmospheric trace gases and particulate matters. By using the combination of the Moderate Resolution Imaging Spectroradiometer (MODIS), the result showed that (27,817) fire hotspots (FHS) occurred between 2005 and 2009 in Thailand and such kinds of particle emissions such as CO_2, CO, CH_4, N_2O, $PM_{2.5}$, PM_{10}, BC, and OC were calculated from forest fires. Similarly, open burning is also a critical source of atmospheric particle emissions in the South East Asian Region. Thus, researchers are being studied about those issues and intensively considered to reduce particulate matters. $PM_{2.5}$ was produced from the open burning of agricultural waste and forest fire as well. From the elemental analysis of $PM_{2.5}$ samples in Chiang Mai Province, K, Mg, Al, and Fe as the major elements were found in the samples emitted from biomass burning such as open burning of agricultural waste and forest fire by using mini volume air samplers in 2013. Then, the concentrations of the elements in the PM_{10} of the ambient air samples highly related to the PM_{10} from the biomass combustion of leaves from agricultural and forest plants such as teak, yangna, and corn leaves [13-15].

The objectives of this research are to investigate the physical and chemical characteristics of biomass burning particles. Besides, morphology and different nanostructures of biomass soot and residual ash were analyzed by using electron microscopy and energy dispersive X-ray spectroscopy with SEM and TEM and focused on the chemical characteristics of biomass leaf, soot, and residual ash by using TGA analysis.

2. METHODOLOGY

About five kilograms of biomass forest leaves (in nature) samples studied in this article were collected from the region of Ladkrabang, Bangkok, the central part of Thailand. All the leaves were initially dried at normal temperature (35°C) in sunlight for 48 hours. After drying, the samples were burnt by using a small burner at an uncontrolled temperature under atmospheric pressure in the open air until all the biomass leaves turn into complete combustion. The particulate matters (PMs) were collected from the trapping equipment installed at the top of the small burner. After complete combustion of the biomass, residual ash which has the visual appearance of silvery grey as powder sample was obtained at the bottom of the biomass small burner. Then it was collected by using a spoon consisting of a shallow oval on a long handle as well. Scanning Electron Microscopy (SEM-SU5000) - Energy dispersive X-ray Spectroscopy (SEM-EDS) and Transmission Electron Microscopy (TEM: 2100 Plus) (TEM-EDS) were used to analyze the chemical composition of biomass raw material, PMs, and residual ash. Transmission Electron Microscopy (TEM: 2100 Plus) and ImageJ (image processing method) were used to characterize the morphology, nanostructure and single primary particle size distribution of biomass PMs and residual ash. The oxidation kinetics of biomass forest leaf, PMs and residual ash was studied by using thermogravimetric analysis (TGA: NETZSCH STA 449F5) under the condition of temperature increasing rate of 10°C per minute in the temperature range of 25°C to 700°C with pure air.

3. RESULTS AND DISCUSSION

Figure 1(a) and (b) show the scanning electron microscopy images of biomass forest leaf with details of morphological aspects in the microstructure. The structures of biomass leaf are also clearly seen by SEM images. Transmission electron microscopy image analysis was conducted to investigate the nanostructures of biomass forest leaves soot and residual ash. Figure 2(a) and (b) show the TEM images of nanostructure of biomass soot fine particles and single primary particles had aggregated each other with similar morphology to become an agglomerate structure of soot nanoparticles. Nanostructure of biomass residual ash fine particles described in Figs. 2(c) and (d) were observed with transmission electron microscopy to compare with the nanostructure of soot fine particles with two different magnifications such as x15k and x30k, respectively. The results show that the morphology of the nanostructure of soot fine particles was not significantly different compared to the nanostructure of biomass leaves ash fine particles. However, it was found that biomass leaves ash fine particles are possessing a smooth surface morphology, and some parts of ash nanoparticles are irregular shapes in size.

Figure 3(a) and (b) show the TEM images of single primary particles of nanostructure of biomass forest leaves soot and residual ash. The nanostructure of a single primary particle of soot is a spherical shape and mainly composed of curve lines as carbon crystallites and nanostructure of biomass leaves ash particle which is non-spherical shape mainly composed of parallel straight-line hatch patterns. Figs. 4(a) and (b) show the nanostructure of biomass soot fine particles and the single primary particle size distribution of biomass soot. The several units of single nanoparticles of soot were measured by using the TEM image processing method to get the results of the size distribution of soot nanoparticles. The diameters of single primary nanoparticle of soot are in the range of 20 nm ~ 55 nm, and the average diameter size of single primary nanoparticles soot from biomass combustion is approximately 36 nm, respectively.

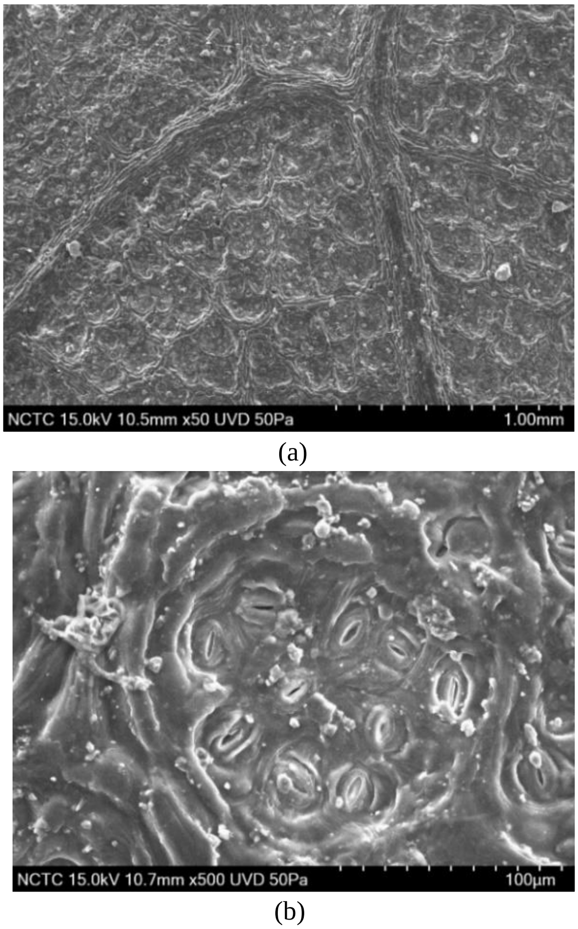
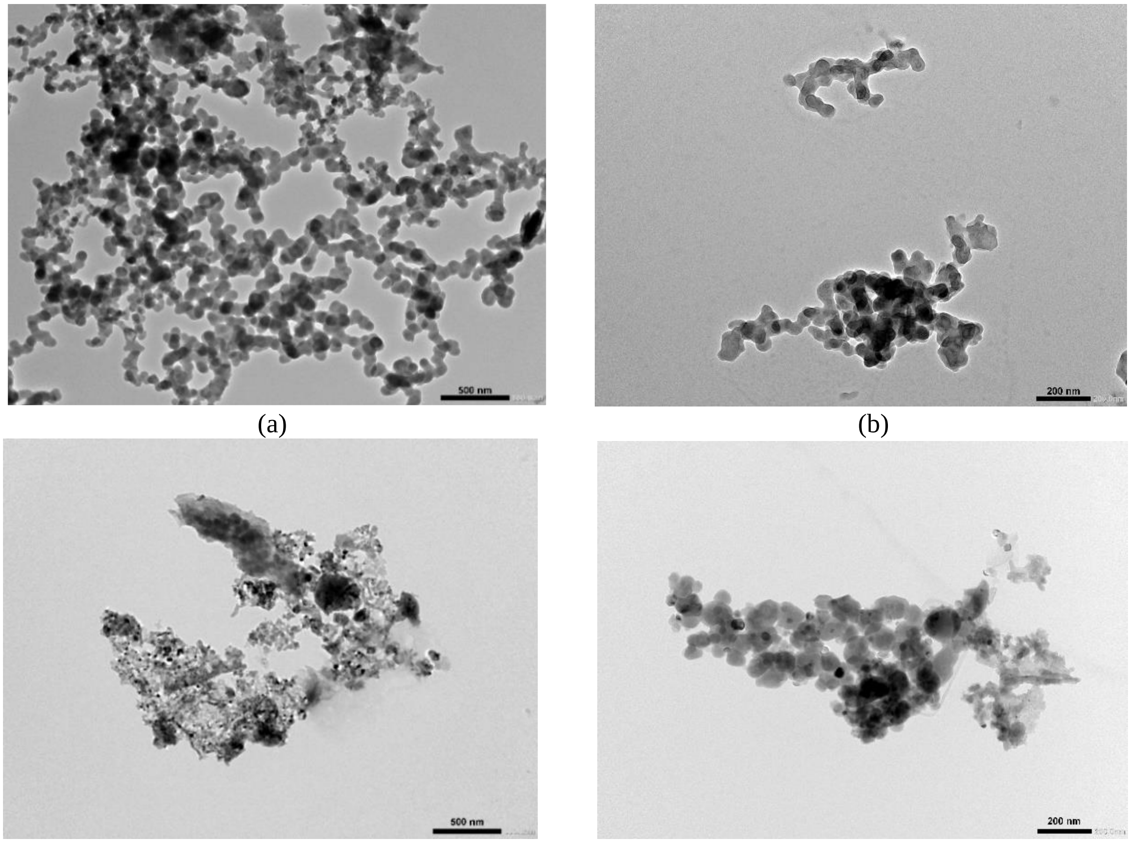


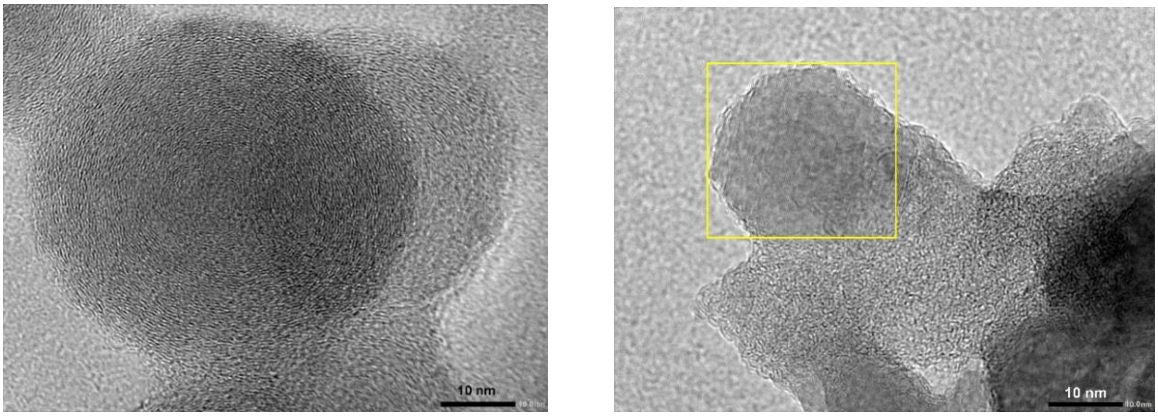
Fig. 1. SEM images of biomass forest leaf microstructure in magnifications with (a) x50 times, and (b) x500 times.



(a) (b)

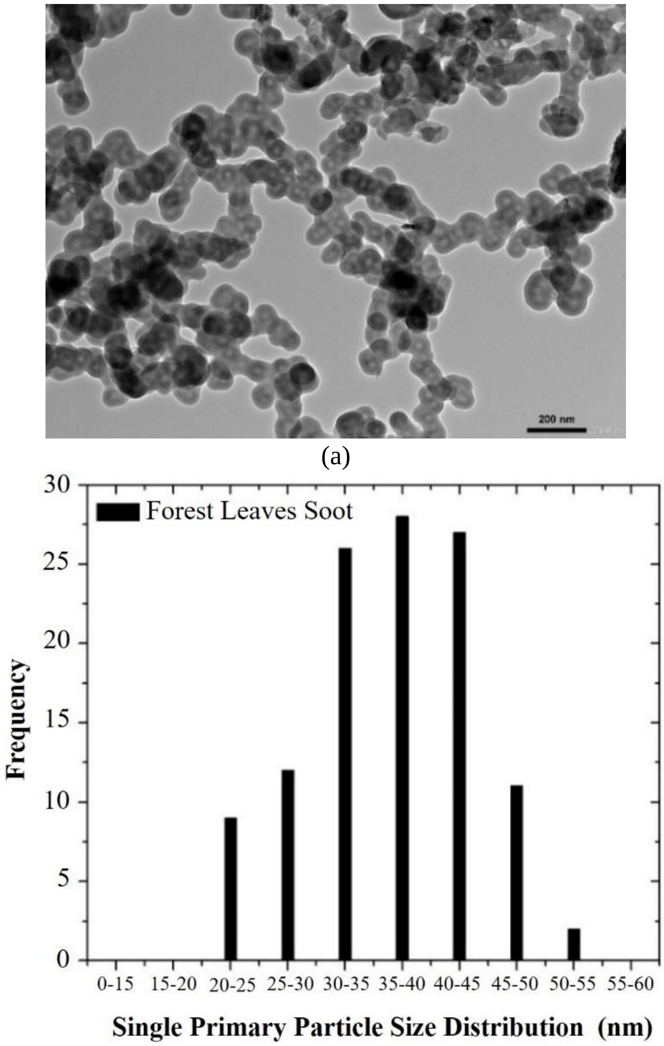
(c) (d)

Fig. 2. TEM images of nanostructure of biomass leaves (a) soot fine particles (magnified: x15k), (b) soot fine particles (magnified: x30k), (c) residual ash fine particles (magnified: x15k), and (d) residual ash fine particles (magnified: x30k) from biomass combustion.



(a) (b)

Fig. 3. TEM images of nanostructure of primary particles of (a) soot, and (b) residual ash from biomass combustion in magnification with x800k.



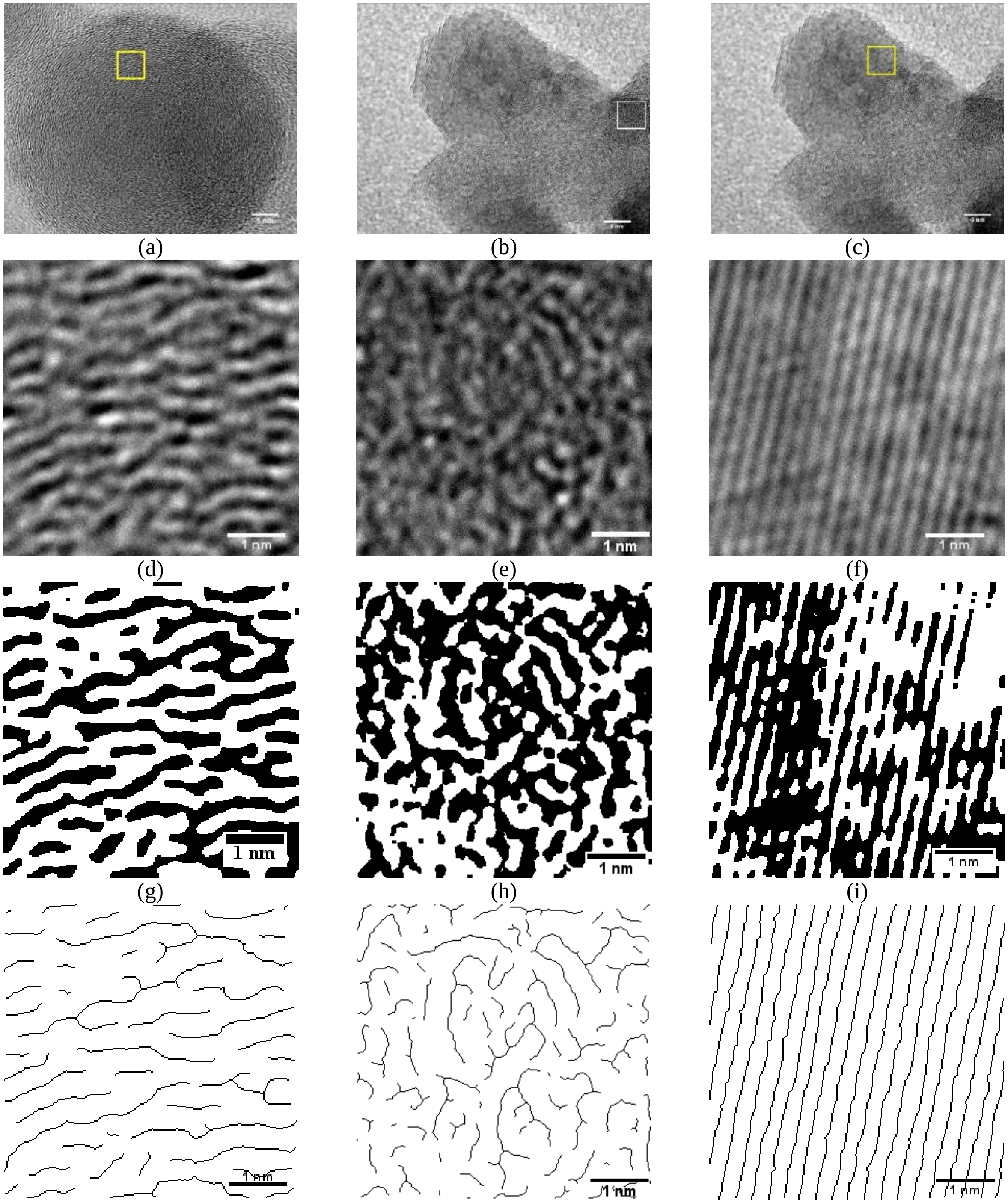
(a)

(b)

Fig. 4. (a) Nanostructure of biomass leaves soot fine particles, and (b) single primary particle size distribution of biomass forest leaves soot.

Figure 5(a-l) show the skeletonized images analysis of biomass leaves soot nanoparticle, soot and ash from residual ash nanoparticle using the TEM image processing method. To investigate the different skeletonized nanostructure of biomass forest leaves soot, residual ash, TEM images were specified in the region, as shown in Fig. 5(a-c), and cropped into (5 nm × 5 nm) scales and transformed into a binary black and white images, and then changed into skeletonized images by using ImageJ software and step by step TEM images processing analysis as described in Fig. 5. In the TEM image of residual ash nanoparticle, it was clearly seen that soot and ash are integrated into the same agglomeration particles, as shown in Fig. 5(b) and (c). According to the skeletonized images of biomass soot and ash, it was mainly composed of curve lines carbon crystallites in soot, and straight-line hatch patterns in ash crystal and the inter-planar spacing of fringes of soot and ash crystallites is about 0.36 nm and 0.28 nm, respectively.

The mass conversion of biomass forest leaves soot compared to the biomass raw material (leaf), and residual ash by using the non-isothermal method, as described in Fig. 6. TGA analysis was conducted with pure air, and the temperature rate is from 25℃ to 700℃. The results of mass conversion could be divided into three regions. In the first region, it could be considered the moisture vaporization zone with a small decreasing of weight loss in the temperature range of 100 to 250℃ for biomass leaf, soot, and residual ash. In the second region, unburned hydrocarbon and carbon are oxidized from 250 to 500℃. The third region is the pure carbon oxidization region at a temperature of 500 to 600℃ with complete combustion for biomass soot. Besides, incombustible metallic ash was found until 700 ℃ both biomass leaf and residual ash.



(a) (b) (c)
(d) (e) (f)
(g) (h) (i)
(j) (k) (l)

Fig. 5. TEM images of nanostructure of a specified region of biomass (a) soot nanoparticle, (b-c) soot and ash from residual ash nanoparticle, (5×5) nm^2 cropped images of (d) soot crystal, (e-f) soot and ash crystal of residual ash nanoparticle, black and white images of (g) soot crystal, (h-i) soot and ash crystal of residual ash nanoparticle, skeletonized images of (j) soot crystal, (k-l) soot and ash crystal of residual ash nanoparticle from biomass combustion.

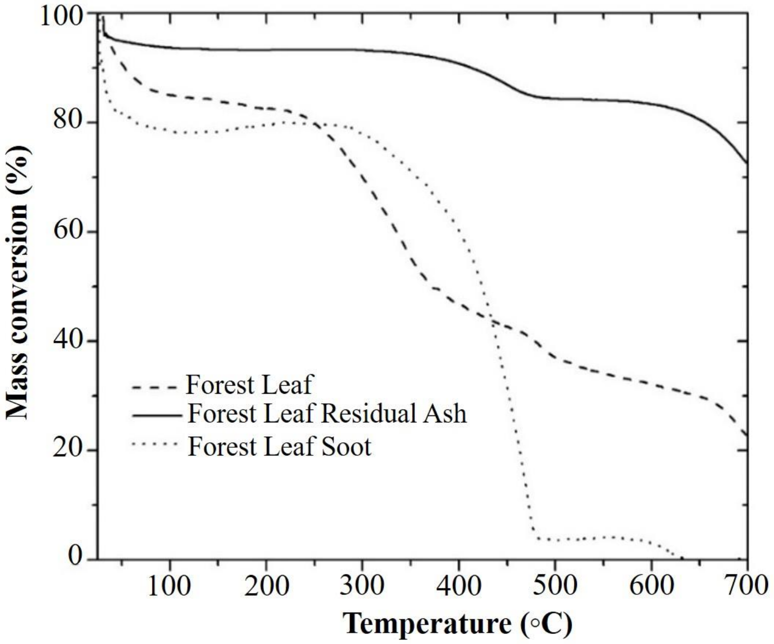


Fig. 6. Thermogravimetric analysis (TGA) of mass conversion of biomass forest leaf, residual ash and soot using the non-isothermal method with pure air (25 °C to 700 °C).

Elemental compositions of biomass forest leaf and PMs were obtained through energy dispersive X-ray spectroscopy with SEM-EDS analysis and TEM-EDS analysis, respectively. SEM-EDS analysis was conducted to determine the chemical compositions of biomass raw material, and it was found that the elements are Carbon (C), Oxygen (O), Magnesium (Mg), Aluminum (Al), Silicon (Si), Sulphur (S), Potassium (K), and Calcium (Ca) as described in Fig. 7(a). TEM-EDS analysis was introduced to investigate the elemental composition of forest leaves PMs and residual ash as described in Figs. 7(b), and (c). According to the elemental analysis, about 65% of carbon fraction was found in biomass raw material before burning while 95% of carbon fraction in forest leaf soot and 84% in ash after burning as well. However, chemical compositions of residual ash particles contain not only Carbon (C) but also especially Magnesium (Mg), Silicon (Si) and Iron (Fe) among the ash-forming elements such as Al, Si, Ca, Fe, K, Mg, Na, and P in biomass. The weight percentage of the chemical composition of biomass leaf, soot, and residual ash are described in Table 1.

Table 1: Elemental analysis of biomass leaf, soot, and residual ash using SEM-EDS and TEM-EDS

	Composition (%)		
Element	**Leaf**	**Soot**	**Residual ash**
C	64.50	95.92	84.28
O	33.10	2.53	12.83
Mg	0.20	-	2.06
Si	0.80	0.86	0.39
Mn	-	-	0.01
Fe	-	0.01	0.03
Cu	-	0.30	0.40
N	-	0.27	-
Al	0.20	0.07	-
Cr	-	0.04	-
Ca	0.70	-	-
K	0.30	-	-
S	0.10	-	-

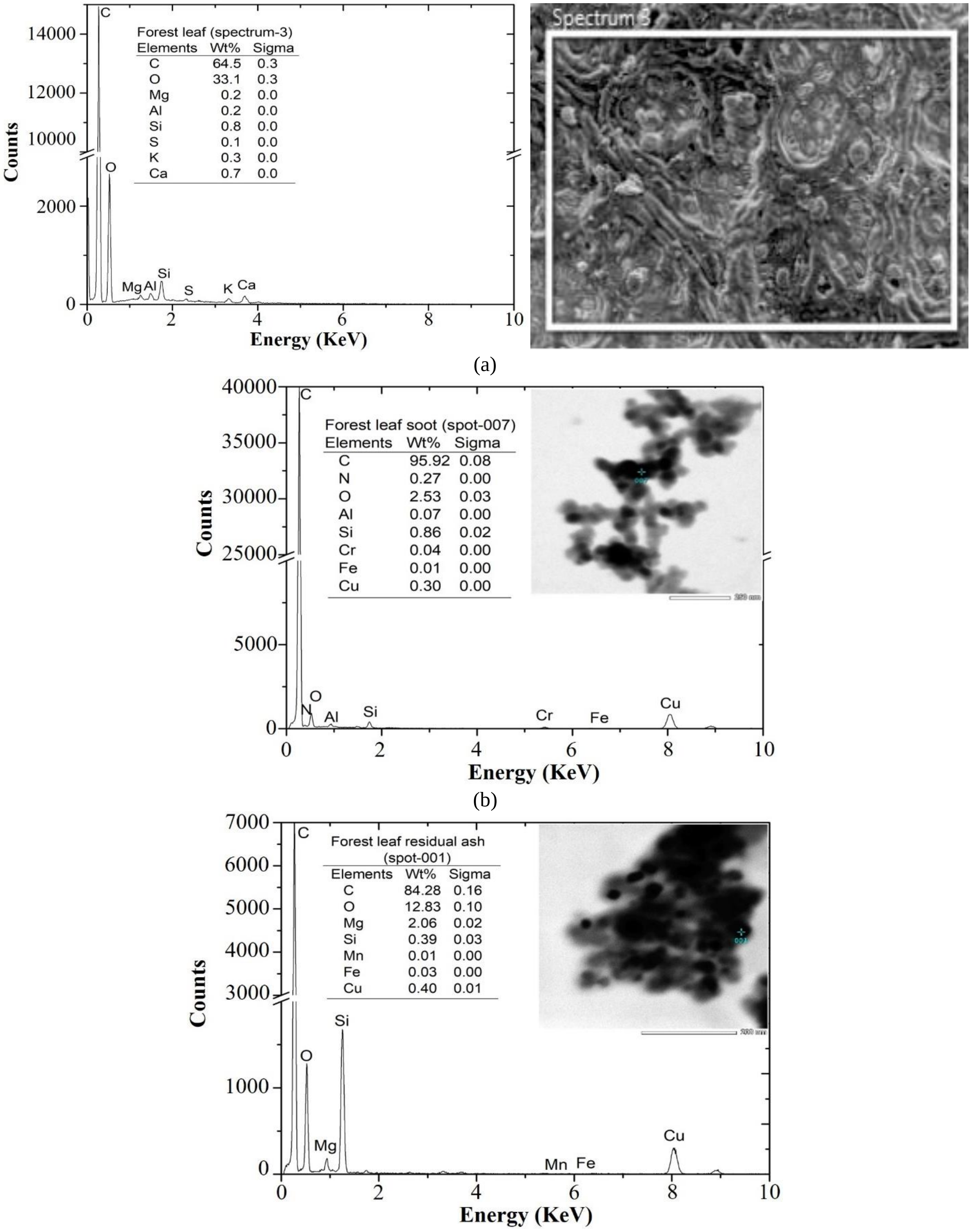


Fig. 7. Elemental analysis of (a) biomass forest leaf (SEM-EDS), (b) biomass soot (TEM-EDS) and (c) biomass residual ash (TEM-EDS).

4. CONCLUSION

Morphology, nanostructure, single primary particles size distribution, chemical composition and oxidation kinetics were successfully discussed by using electron microscopy, energy dispersive X-ray spectroscopy, and thermogravimetric analysis. According to the results of electron microscopy, the morphology of the nanostructures of biomass leaves soot are not significantly different compared to the nanostructure of residual ash while residual ash particles are possessing a smooth surface morphology, and some parts of residual ash are irregular shapes in size. The single primary nanoparticles of leaves soot are spherical shape composed of curve line carbon crystallites and residual ash are non-spherical shapes composed of parallel straight-line hatch patterns. Results of the particle size distribution of soot, the diameters of single primary nanoparticle are in the range of 20 nm ~ 55 nm, and the average diameter is about 36 nm, respectively. Elemental analysis of nanoparticles, biomass forest leaves PMs are mainly composed of Carbon (C) approximately 95%. At the same time, chemical compositions of biomass residual ash contain not only Carbon (C) but also especially Magnesium (Mg), Silicon (Si) and Iron (Fe) among the ash-forming elements such as Aluminium (Al), Silicon (Si), Calcium (Ca), Iron (Fe), Potassium (K), Magnesium (Mg), Sodium (Na) and Phosphorus (P) in biomass. The results of TGA analysis, biomass PMs are easier to oxide than biomass residual ash because of the unburned hydrocarbon, and incombustible metallic ash of residual ash. Also, pure carbon oxidization was occurred in temperature range about 500 to 650°C with complete combustion for biomass soot.

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