CHAPTER 5

PHYSICAL AND CHEMICAL PROPERTIES OF BIOMASS FUEL, TOTAL PARTICULATE MATTER, CARBONACEOUS AEROSOLS AND RESIDUES AFFER BURNING

5.1 Materials and Methods

5.1.1 Sample Preparation for Elemental Compositional Analysis

The biomass fuel, as seedlings, grasses, shrubs, climbers, herbs and litters (leaf and twig) was collected from the field and the mass determined using the gravimetric method, consisting in measuring the fresh weight of the biomass just after its cut. Then, biomass fuel samples were oven-dried at 70-80 °C for at least 24 h or weight constant, and weighted again to determine the fuel moisture content and the dry weight.

Biomass fuels were cut (SM 2000 model, Retsch, Germany) and ground (PM_{10} model, Retsch, Germany) until powder form or sieve size selected less than 100 μm. All of samples were contained in desiccator at least 24 h before quantify the chemical composition.

A mixture of ash and charred leaf was collected from the field, then the ash composition is was sieved and a big piece of charred leaves was also separated from the unburned samples by forceps, a mixture of ash and charred leaves were ground and stored in a desiccator for 24 h before quantify the carbon content and trace elemental composition.

5.1.2 Elemental Composition Analysis

Elemental component as nitrogen (N), carbon (C), hydrogen (H) and sulfur (S) in biomass and particulate matter were analyzed by the OEA analyzer (FlashEA1112, NC soil model, Thermo Finnigan, Italy). The principle of an OEA analyzer includes combustion, reduction, and GC separation with thermal conductivity detector (Appendix B). The homogeneous of sample was cut and ground in the sample preparation step that is weighed in tin capsule and introduced into the combustion reactor. The oven containing reactor, the air is purged by helium atmosphere for 12 sec, then heated to temperature set up (Appendix B).

5.1.3 Ash Content of Biomass Fuel

Ash in biomass fuel analyses for calorific value calculation was obtained based on reapproved ASTM standard method for ash in biomass E 1755-01 (ASTM, 2007). Biomass fuel samples were cut by cutting mill (SM 2000 model, Retsch, Germany) after oven-dried at 70-80 °C for 24 h, then contained in desiccator for 24 h. The sample container was use crucibles that were heating at 575±25°C for 3 h by furnace (Carbolite 3216P1, RHF 16/15 model, Unite Kingdom), cool to room temperature in a desiccator and weigh by 4 digits balance, record the crucible weigh. After that the samples were use 2-3 g contain in the crucible, weigh and record (crucible plus sample mass) and heat up to 250°C at a rate of 10K/min, then hold for 30 min and increasing the temperature to 575±25°C for 3 h, cool to room temperature in a desiccator and weigh by balance and record the final mass (crucible plus ash mass). Mass percent of ash was estimated by Equation 5.5.

$$\%\,ash = \left[\frac{m_{ash} - m_{cont}}{m_s}\right] \times 100 \qquad \text{Equation 5.5}$$

where: *%ash* is the mass percent of ash, based on 105 °C oven-dried mass of the sample, m_{ash} is the mass of ash and container (g), m_{cont} is the tare mass of container (g), m_s is the mass of moisture-free solids in the prepared biomass sample (g).

5.1.4 Calorific Value Determination

The elemental component in biomass was used to calculate the gross calorific value (GCV) or high heating values was defined by CEN/TS 14918 which is the solid biofuels method for determination of calorific value. This method represents the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a calorimetric bomb under the conditions specified (CEN/TS 14918:2005). On the basis of the GCV and the elemental composition, the net calorific value (NCV) was calculated. CEN/TS 14918 defines NCV at a constant pressure as the absolute value of the specific heat (enthalpy) of combustion, in joules, for unit mass of the biofuel burned in oxygen at constant pressure under such conditions that all the water of the reaction products remains as water vapour (at 0.1 MPa). The calorific value of the equation of Friedl (Friedl, 2005) is in kJ/kg.

$$GCV = 5.22C^2 - 319C - 1647H + 38.6C \times H + 133N + 21028 \qquad \text{Equation 5.3}$$

The net calorific values (NCV) was estimated from GCV by the equation this below,

$$NCV = GCV - 212.2H - 0.8(O + N). \qquad \text{Equation 5.4}$$

5.1.5 Trace Elemental Analysis

Samples of biomass (i.e. leaf litter, twig, and seedling) and residues after burning were weighed with a microbalance after cutting and grinding. Weighing approximately 0.2 to 0.5 g of sample powder form. Each sample was placed in a teflon container with suprapure grade of re-distilled concentrated 8mL HNO_3, 1mL of re-distilled concentrated HCl and 2mL of concentrated H_2O_2. Prior digest by microwave digestion (Anton Paar, Microwave 3000 model), the containers was sealed and shacked then place in a microwave digester with the condition that showed in Appendix B.

5.1.6 Morphology of Total Particulate Matter (TPM)

Quartz filters of 47 mm diameter (Pall Life Sciences, USA.) were preheated at 800°C for 5h (Cao *et al.*, 2008) then placed in desiccator for 24h, weighting before use to collect particulate matter from forest fires. Smoke flow through the filter contained in the open-faced of stainless filter holder (Pall Life Sciences, USA.) under a total flow rate of 5LPM. Each particulate emissions sample was taken in the plume until complete burn down indicated by no further visible smoke emissions. Particulates collected on the filter were contained in desiccators for 24 h before weigh and quantify the chemical composition.

The morphology of the particulate matter collected on quartz filters were measured by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX). Samples were punched and placed on a stub, coated with Au/Pd alloy for 100-200 s and then transfer to the SEM-EDX. Micrographs were taken at 20 Kv with working distance of 15 nm. Identification and characterization of BC were performed with a high-resolution scanning electron microscope (JEOL, Model: ISM-S410LV, JAPAN). Black carbon was determined by O_C/C ratios. An approximation of the atomic percentage of oxygen bound to carbon (O_C) was therefore assessed based on Brodowski et al., 2005 as follows:

$$\%O_C = \%O-(\%Na\times0.5 + \%Mg\times1 + \%Al\times1.5 + \%Si\times2 + \%K\times0.5 + \%Ca\times1 + \%Fe\times1.176 + \%P\times2.5) \qquad \text{Equation 5.6}$$

5.1.7 Carbonaceous Aerosol Quantification

In this study, only black carbon measurements using a real-time analyzer based on optical method for determination, i.e. Aethalometer, were conducted to determine BC content. Actually, TPM were also collected on quartz filters for the determination of TC, OC and BC contents by thermal method at the laboratory. However, problems of filter saturation due to high concentration in the plume occurred during the sampling. Therefore, these filter samples were discarded from the quantification. However, TC is assumed to present 60% of the $PM_{2.5}$ total mass (Ward *et al.*, 1992) that can be written as:

$$TC = 60\% \times PM_{2.5} \qquad \text{Equation 5.7}$$

where: TC is total carbon, mg/m^3, $PM_{2.5}$ is concentrations of particulate matter with aerodynamic diameter lesser than 2.5 micrometers, mg/m^3 and 60% is a factor value of carbon content in $PM_{2.5}$ (Ward *et al.*, 1992).

5.2 Results and Discussion

5.2.1 Proximate and Ultimate Composition

The elemental component in biomass fuel as nitrogen, carbon, and hydrogen was analyzed by OEA analyzer. The results are illustrated in Table 5.1. Ash content in biomass fuels was determined based on ASTM standard method for ash in biomass E 1755-01 (Reapproved 2007). Oxygen is estimated from the difference between the sum of the carbon (C), hydrogen (H), sulfur (S), nitrogen (N) and ash concentrations (in wt% (d.b.)) and 100%.

Table 5.1 Elemental and ash content of biomass fuel of DDF and MDF plots

Forest type	Category	Elemental and Ash (%)				
		N	C	H	O	Ash
DDF	Leaf litter	0.81	46.00±0.14	6.06±0.14	41.13	6.31±0.28
	Twig	0.57	43.49±0.09	5.53±0.10	43.74	6.67±0.13
	Seedling	1.56±0.02	44.35±0.51	7.92±0.05	36.76	9.41±0.43
	Understory	0.94±0.01	43.32±0.09	6.10±0.11	42.79	6.85±0.23
MDF	Leaf litter	1.09	37.31±0.44	5.58±0.06	36.27	19.75±0.49
	Twig	0.59±0.03	46.00±0.04	6.06±0.14	42.25	5.10±0.03
	Seedling	1.04±0.01	43.09±0.07	6.06±0.05	39.55	10.26±0.03
	Understory	1.25±0.01	42.85±0.14	6.15±0.07	38.00	11.75±0.16

In DDF, the elements of N, C and H component of each category (leaf litter, twig, seedling and understory) have the same order of magnitude and also have the same ash values. The understory in MDF is the highest N content. It was showed that N content could be an indication the NO_x emissions. C and O are the main components of all biomass that become oxidized during burning and influence the gross calorific value of the fuel. However, leave litter in DDF is composed the highest of C-content. On the other hand, leaf litter in MDF, C-content is the lowest. In addition, ash content in leaf litter in MDF is the highest.

Table 5.2 Gross calorific values and net calorific value of biomass fuels in DDF and MDF

Forest and fuel types	GCV (kJ/kg)	NCV(kJ/kg)
DDF		
Leaf litter	18,288	16,970
Twig	17,280	16,071
Seedling	17,870	16,159
Understory	17,284	15,955
MDF		
Leaf litter	15,385	14,171
Twig	18,258	16,938
Seedling	17,212	15,894
Understory	17,154	15,817

5.2.2 Calorific Value of Biomass Fuels

The calorific value of leaf litter in DDF and MDF is shown in Table 5.2. Gross calorific value (GCV) and net calorific value (NCV) in biomass fuels were estimated by formula of Friedl (Friedl, 2005). The GCV and NCV of each category in DDF and MDF are based on the element content in Table 5.1. The value of NCV is used to calculate the fireline intensity by Byram (Byram, 1959) formula. Leaves litter in DDF is the highest of NCV, while in MDF. It was showed that the leaf litter in DDF will release the energy higher than leaf litter in MDF. However, not only the NCV value but also the moisture content in biomass fuel that influence for the combustion phase.

Table 5.3 Trace elemental composition (% of mass) of biomass fuel and a mixture of ash and charred leaf (residues after burned) in DDF

Element (symbol)	Elemental composition (%of mass)			
	Leaf litter	Twig	Seedling	Residues after burned
Sodium (Na)	0.0017	ND	ND	0.0224
Magnesium (Mg)	0.2728	0.9881	0.2418	0.6333
Aluminum (Al)	0.4286	0.1397	0.0437	0.9919
Potassium (K)	0.4861	0.2111	1.9127	1.4829
Calcium (Ca)	4.7120	18.1517	3.9468	5.8885
Chromium (Cr)	0.0823	0.0259	0.0035	0.5108
Manganese (Mn)	0.0484	0.0638	0.0088	0.1216
Iron (Fe)	0.8992	0.4528	0.0777	5.9319
Cobalt (Co)	0.0001	ND	ND	0.0009
Nickel (Ni)	0.0015	0.0008	0.0001	0.0071
Copper (Cu)	0.0012	0.0006	0.0006	0.0056
Zinc (Zn)	0.0085	0.0036	0.0004	0.0048
Gallium (Ga)	0.0003	0.0001	ND	0.0006
Arsenic (As)	0.0001	ND	ND	0.0002
Rubidium (Rb)	0.0041	ND	0.0063	0.0107
Strontium (Sr)	0.0023	0.0212	ND	0.0048
Yttrium (Y)	0.0105	0.0683	0.0403	ND
Rhodium/Rh	0.1750	ND	ND	ND
Cesium/Cs	ND	ND	ND	0.0003
Barium/Ba	0.0003	0.0036	0.0002	0.0028
Lead/Pb	0.0002	0.0001	ND	0.0004

ND means not detected

Table 5.4 Trace elemental composition (% of mass) in biomass fuel and a mixture of ash and charred leaf (residues after burned) in MDF

Element (symbol)	Elemental component (% of mass)			
	Leaf litter	Twig	Seedling	Residues after burned
Sodium (Na)	0.0161	0.0000	0.0066	0.1829
Magnesium (Mg)	0.2172	0.1580	0.2230	0.2858
Aluminum (Al)	0.5170	0.1083	0.0164	2.1222
Potassium (K)	0.2767	0.1578	1.7572	1.4679
Calcium (Ca)	3.1002	7.9230	4.4630	3.2153
Chromium (Cr)	0.0496	0.0141	0.0055	0.7297
Manganese (Mn)	0.0286	0.0065	0.0100	0.0826
Iron (Fe)	0.7372	0.2444	0.1027	8.5397
Cobalt (Co)	ND	ND	ND	0.0014
Nickel (Ni)	0.0008	0.0002	0.0004	0.0103
Copper (Cu)	0.0013	0.0039	0.0010	0.0078
Zinc (Zn)	0.0058	ND	0.0017	0.0060
Gallium (Ga)	0.0003	0.0001	ND	0.0011
Arsenic (As)	ND	ND	ND	0.0005
Rubidium (Rb)	ND	ND	0.0039	0.0168
Strontium (Sr)	0.0031	0.0163	NM	0.0054
Yttrium (Y)	0.0061	0.0750	0.1161	ND
Rhodium (Rh)	0.1827	ND	ND	ND
Cesium (Cs)	ND	ND	ND	0.0041
Barium (Ba)	0.0008	0.0007	0.0005	0.0046
Lead (Pb)	0.0002	ND	ND	0.0007

ND means not detected

5.2.3 Trace Elemental Composition of Biomass Fuel and Residues After Burned

In DDF, the dominant of elemental components in leaf litters are Mg, Al, K, Ca, Fe and Rh (Table 5.3). Especially Ca and K are the mineral composition in plant tissues. The major elemental composition in leaves from MDF is composed of the same type in DDF. Trace element contents in twig both DDF and MDF are dominant type in good agreement as Mg, Al, K, Ca and Fe. However, Mg, K and Ca are the trace elements dominant in seedling of DDF. On the other hand, not only Mg, K and Ca but also Fe and Y are the trace elemental contents in seedlings of MDF. The dominant trace elements in ash and charred leaves of both DDF and MDF are Mg, Al, K, Ca, and Fe but Na was also found in ash and charred leaves of MDF (Tables 5.3 and 5.4). Understory and seedling in both forest types are composed the major element of Ca and K that they are the one part composition in cell wall of plant tissue. It is also found the heavy metal as Pb, Cr, Cu, As and Zn in leaf litter of both forest type except, As not found in leave litter and also seedling and ash and charred leaves of MDF. However, As was found in leaf litter and ash and charred leaves of DDF only.

Table 5.5 Trace elemental composition of total particulate matter (TPM), % of mass

Element/Symbol	Chaiyo et al., 2011		Yamasoe et al., 2000		Schmidl et al., 2008
	Tropical deciduous forest		Tropical forest		Leaves
	DDF	MDF	Flaming	Smoldering	
Aluminum/Al	0.0144	0.0430	0.2±0.2	0.6±0.5	0.011-0.024
Arsenic/As	0.0069	<0.0001	-	-	0.0010-0.0015
Calcium/Ca	1.5555	0.2936	0.008±0.003	0.06±0.04	0.143-0.378
Chlorine/Cl	0.3273	0.5819	0.3±0.2	0.2±0.2	0.1400-0.353
Cupper/Cu	0.0164	0.0007	0.004±0.001	0.003±0.002	0.0001-0.0285
Iron/Fe	1.0256	0.0280	0.031±0.009	0.048±0.029	0.0079-0.0493
Lead/Pb	0.0089	0.0023	-	-	0.0015-0.0028
Magnesium/Mg	0.9125	0.0527	0.025±0.022	0.025±0.028	0.006-0.0716
Manganese/Mn	0.0130	0.0012	0.005±0.002	0.003±0.001	0.0001-0.0156
Nickel/Ni	0.0415	0.0025	0.004±0.001	0.003±0.002	0.0004-0.0116
Potassium/K	1.1242	2.0649	0.8±0.6	0.4±0.3	0.174-0.8850
Phosphorus/P	ND	ND	0.045±0.007	0.036±0.014	-
Selenium/Se	0.0091	0.0002	0.0028±0.0024	0.002±0.0009	-
Sodium/Na	0.8749	0.0544	0.014±0.008	0.014±0.009	-
Titanium/Ti	0.0004	0.0004	-	0.008±0.003	0.0001-0.006
Zinc/Zn	0.0116	0.0041	0.007±0.004	0.004±0.002	0.0148-0.0790

ND means not detected

5.2.4 Trace Elemental Composition in Total Particulate Matter (TPM)

In order to simulate TPM samples from prescribed fires. In this study, TPM collected on filters cannot be quantifying trace element component to the atmosphere due to the failure of equipment field during emission air sampling. Therefore, in estimation the amount of trace element in TPM emitted from fire that cannot do both DDF and MDF. For these reasons, the results of the other research used to obtain an overview of trace element component in TPM from forest fire (Table 5.5). It was found that the TPM emitted from biomass fuels in DDF and MDF in Chiangmai province is composed of the major trace element as Na, Mg, Cl, K, Ca and Fe. The results consistent with the other research that shown in Table 5.5, some of elements as Ca, Fe and K are higher than the other research that suggested these elements should measure by the other technique. The quantification of trace elemental component detected in leaves litter of this study suggested that the same type of similar elements of this research. But there are significant differences in the amount released to the atmosphere, depending on the biomass fuel properties and combustion phase so on.

5.2.5 Morphology of Total Particulate Matter (TPM)

TPM colours collected on the filters is grey to dark and brown colours in DDF and MDF, respectively (Figures 5.1 and 5.2). It was show that the smoke release from biomass burning is different the combution phase and high vary of smog into the atmosphere . However, the TPM collected on filter is very saturated and thick due to the pump was shut down that cannot be measured the BC by optical transmittance (OT) analyzer. In additon, the OT cannot measure because the filter color is over range of detected. The TPM colour in both DDF and MDF in this study is in good agreement with Chaiyo et al. (Chaiyo *et al.*, 2011) to conduct TPM from the burning of biomas fuel in Chiangmai Province.

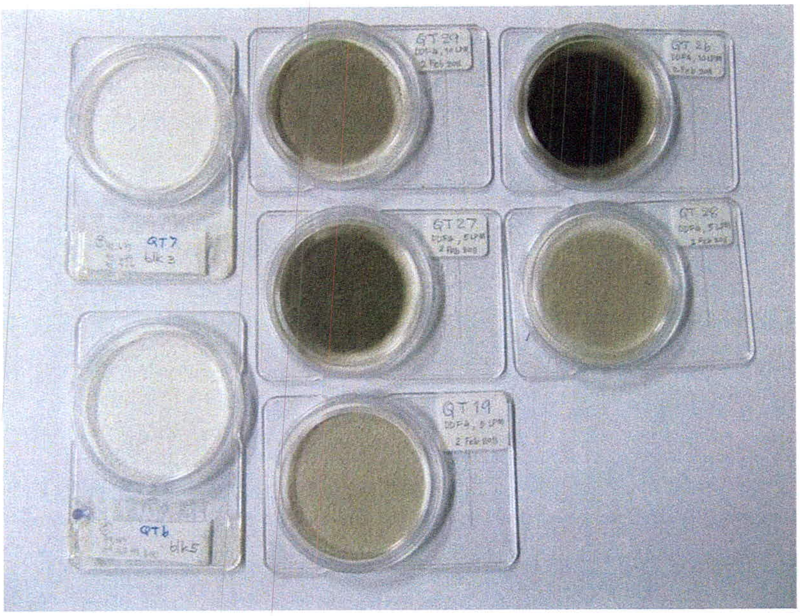

Figure 5.1 Characterization of TPM collected on quartz filters from prescribed burning of DDF

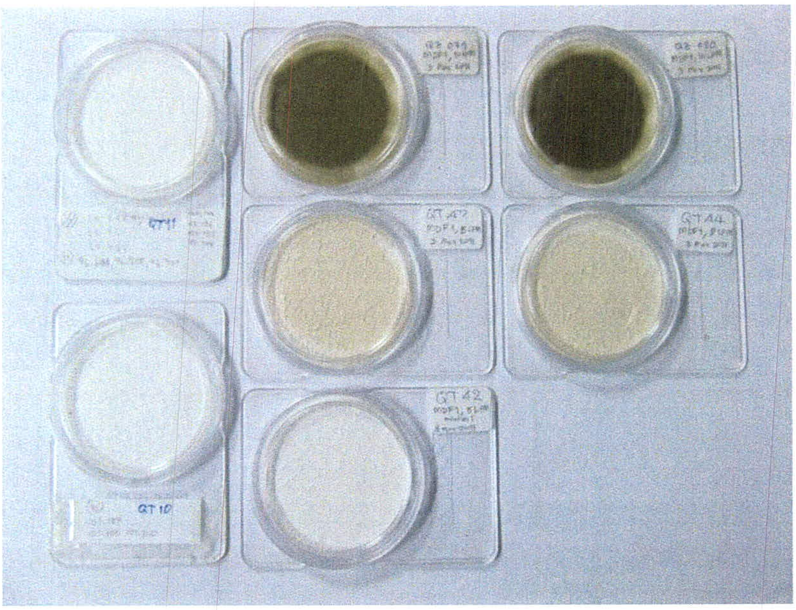

Figure 5.2 Characterization of TPM collected on quartz filters from prescribed burning of MDF

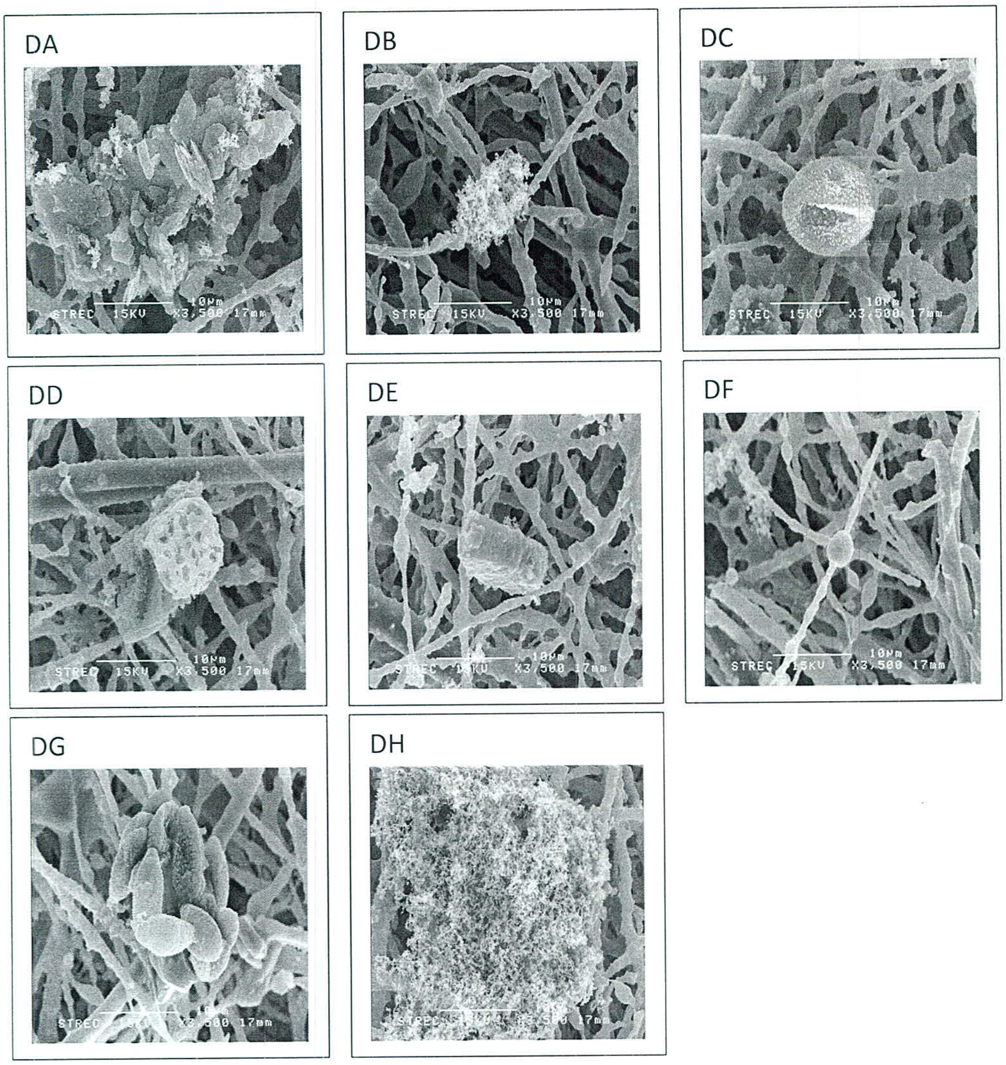

Figure 5.3 SEM micrographs of particulate matter collected on quartz filters from DDF prescribed fires

The SEM micrographs of TPM have varied morphological types as shown Figures 5.3. The O_C/C ratio <0.5 is use to identified black carbon (Glaser *et al.*, 2000, 2001). The micrographs from burning of DDF are 8 shape forms (Figure 5.3). DA micrograph is the highest micrographs found in DDF filter punched 10mm diameter characteristic, followed by DB, DH and DG micrographs, respectively. Black carbon was identified by the ratios of O_C/C, we found that almost all micrographs in DDF are the black carbon whereas DC shape.

However, the SEM micrographs show not only DDF fires but also other sources (i.e. dust). The important element released from biomass burning is composed of the highest of potassium followed by chlorine, sulfur, calcium and aluminum, respectively

(Yamasoe *et al*., 2000; Ward *et al*., 1992). In this study, the key element was used the potassium to identify the micrograph of TPM released from forest fires. DC, DD, DE and DG micrographs suggested that they are the carbonaceous aerosols emitted from DDF fires. DD, DE and DG micrographs are the black carbon and DC micrograph is the organic carbon that identification based on the O_C/C ratios.

Table 5.6 Elemental compositions by SEM of TPM from DDF prescribed fires

Shape type	Amount	Element (%)									O_C/C
		C	O	Al	Si	Cl	K	Ca	Mg	Fe	
DA	10	44.75	35.22	7.28	10.75	0.83	-	0.18	-	1.00	0.032
DB	7	53.93	36.99	-	9.08	-	-	-	-	-	0.349
DC	2	59.37	38.07	-	1.11	1.00	0.45	-	-	-	0.600
DD	2	60.79	33.00	-	5.18	0.24	0.46	0.33	-	-	0.363
DE	2	40.66	23.97	2.75	29.00	-	1.42	2.20	-	-	<0.00
DF	2	68.19	27.98	-	3.83	-	-	-	-	-	0.298
DG	3	50.29	37.22	-	7.47	2.17	1.87	0.98	-	-	0.405
DH	5	56.56	32.40	-	11.03	-	-	-	-	-	0.183

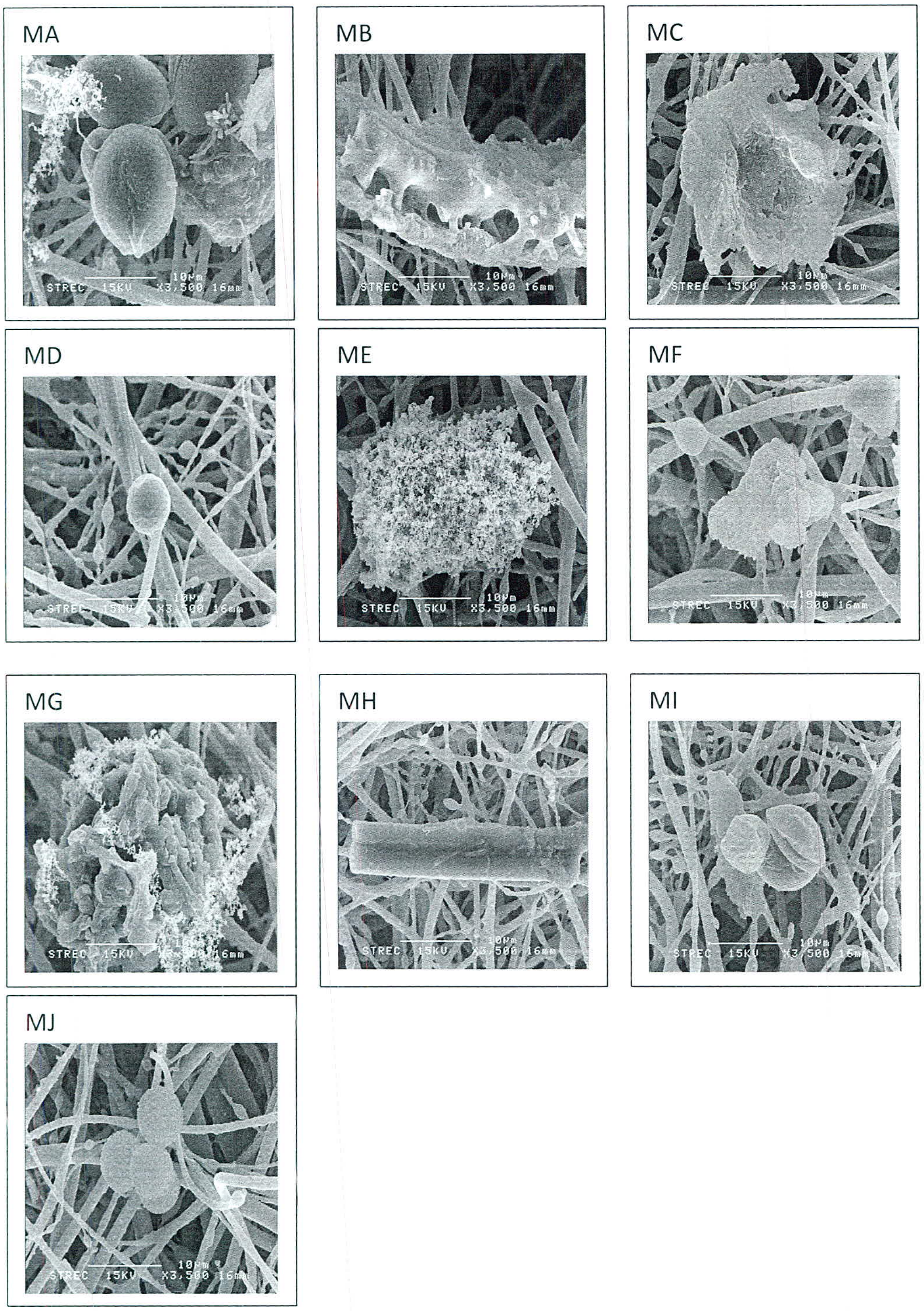

Figure 5.4 SEM micrographs of particulate matter collected on quartz filters from MDF prescribed fires

Table 5.7 Elemental compositions by SEM of TPM from MDF prescribed fires

Shape type	Amount	Element (%)									O_C/C
		C	O	Al	Si	Cl	K	Ca	Mg	Fe	
MA	3	70.28	27.34	-	0.94	0.83	0.61	-		-	0.358
MB	3	21.07	56.71	-	22.22	-	-	-	-	-	0.490
MC	4	45.36	44.42	0.28	7.50	0.30	0.40	0.67	1.08	-	0.639
MD	3	73.28	25.83	-	0.88	-	-	-	-	-	0.328
ME	12	50.33	36.96	-	12.70	-	-	-	-	-	0.230
MF	2	62.34	33.00	-	3.57	-	0.76	0.33	-	-	0.403
MG	8	31.17	50.89	5.36	9.53	0.33	1.09	0.17	0.53	0.92	0.689
MH	3	26.18	51.12	-	22.30	0.18	-	0.22	-	-	0.241
MI	2	58.20	36.64	-	3.38	0.80	0.98	-	-	-	0.505
MJ	2	53.94	41.34	-	3.87	0.37	0.49	-	-	-	0.618

The SEM micrographs in the MDF burning have 10 shapes (Figure 5.6). ME and MG micrographs are the dominant shapes found in MDF. The numbers of black carbon shape are lesser than measured in DDF. Table 5.6 shows the black carbon in MDF have 6 shapes as MA, MD, ME, MF, MI and MJ. According to the filter colors of particulate matter collected on quartz filter from DDF and MDF burning, filter of DDF is gray to dark and brown in MDF (Figures 5.1 and 5.2). In the same manner of SEM micrographs, the O_C/C ratios < 0.5 are used to identify the black carbon morphology (Glaser et al., 2000, 2001) while higher than 0.5 is suggested that organic carbon (Table 5.6). The SEM micrographs are not only from MDF fires but also other sources (i.e. dust). However, the important element released from vegetation fire or biomass burning is composed of the highest of potassium followed by chlorine, sulfur, calcium and aluminum, respectively (Yamasoe *et al.*, 2000; Ward *et al.*, 1992). In this study the key element was used the potassium. In addition, MA, MD, MF, MG, MI and MJ micrographs are associated by potassium, suggest that they are the carbonaceous aerosols emitted from MDF fires. MA and MF micrographs are the black carbon and MD, MG, MI and MJ are the organic carbon that identification based on the O_C/C ratios (Figure 5.4).

The dominant elemental components are associated with the particulate matter emitted from the biomass burning of DDF and MDF as Al, Si, Cl, K, Ca, Mg and Fe. DA and MG micrographs are the highest black carbon morphology released from DDF and MDF, fire, respectively. Black carbon micrographs are higher shape types in DDF than MDF while the organic carbon micrographs found in MDF is higher than DDF that is related to colors of the TPM collected of filter. However, the element species component and the ratios of O_C/C depend on the burning temperature, biomass fuel properties and source.

5.3 Summary of Findings

- The results of carbon estimation in biomass fuels have shown that the carbon content in leafy litters in DDF and MDF were 46.0 and 37.3 % that in DDF is higher than MDF.
- Ash in the leafy litter of MDF is three times higher than in DDF. Therefore the net calorific value in leaf litter was 14,171 and 16,970 kJ/kg in MDF and DDF, respectively.
- The major components of trace element in both DDF and MDF are similar types and the amounts of almost all trace elements are the increase in ash and charred leaves of DDF and MDF.
- TPM collected on filters had different colors. Grey to dark and brown colors in TPM from DDF and MDF, respectively. It is suggested that the BC released from DDF was higher than MDF fire.
- The dominant micrographs of TPM emitted from DDF had 8 forms. DD, DE and DG shapes suggested that the BC morphology and the DC morphology suggested the form of OC from DDF.
- The dominant micrographs of TPM emitted from MDF are 10 forms. MA shape suggested that the BC morphology and the MC, MG, MI and MJ morphologies suggested the forms of OC from MDF fires.
- SEM micrographs in DDF contain more black carbon than MDF. On the other hand, organic carbon is associated to SEM micrographs from MDF higher than from DDF fires.
- The major elemental composition and some fraction of carbon associated to TPM produced from both DDF and MDF fires.