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COMPOSTING OF OIL PALM BIOMASS: FOURIER TRANSFORM-INFRARED AND THERMOGRAVIMETRY ANALYSES

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ABSTRACT

This study investigates the effects of composting conditions on the chemical characteristics of compost from oil palm biomass. Three samples each of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost were collected from three compost plants in Malaysia. The plants employed open windrow composting system. The Fourier transform-infrared spectra and thermogravimetry analysis were used to analyse the samples. It was found that composting resulted in the loss of aliphatic structures by formation of aromatic structures. This led to a stronger intramolecular bond and subsequently increased the stability of compost. The results of the study showed that the use of shredded EFB for composting is the most efficient way to produce compost. It required 55% less amount of time as compared to untreated EFB and 60% less amount of time as compared to treatment without addition of microbes.

Keywords: biodegradation, empty fruit bunches, palm oil mill effluent, Fourier transform-infrared spectroscopy, thermogravimetry analysis.

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INTRODUCTION

Composting is a biodegradation or bioconversion process of organic waste substrate into stable organic end products (Molla *et al.*, 2002). In the Malaysian oil palm industry, composting of empty fruit bunches (EFB) and palm oil mill effluent (POME) has the potential as one of the measures for waste management. The shredded EFB contains 13.7% lignin, 14.8% hemicellulose and 52.8% cellulose (Baharuddin *et al.*, 2010) while the microorganisms in POME provide the biodegradation of EFB which is essentially cellulose (Yahya *et al.*, 2010). POME is a brown slurry containing 4% to 5% organic solids, 0.5% to 1.0% residual oil, approximately 95% water and a high concentration of organic nitrogen (Onyia *et al.*, 2001).

The factors affecting the efficiency of composting of oil palm biomass include the processing temperature, moisture content and frequency of turning. Thambirajah *et al.* (1995) found that the temperature increased rapidly to approximately 75°C within one day and decreased to 40°C after 21 days. The temperature continued to reduce until it reached the ambient temperature. Both mesophilic and thermophilic bacteria showed consistent activity throughout the process. Temperature of piles could be controlled by mixing and turning during composting. Yahya *et al.* (2010) reported that the microbial activity was at its optimum at high temperature. However, the presence of moisture

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influenced the growth and microbial activity. Nayono *et al.* (2010) had reported that moisture content should be within the range of 40% to 60% of the total volume throughout the composting process. Moisture content below the range inhibited the microbial activity while above the range led to anaerobiosis and bad odour. Turning frequency of piles for aeration had been found to affect the process. Wei *et al*. (2000) reported that sufficient aeration was important to supply enough oxygen required by microbes in breaking down the raw materials.

Various studies found that Fourier transform-infrared (FT-IR) spectroscopy (Cuetos *et al.,* 2010; Smidt *et al.,* 2005) and thermogravimetry analysis (TGA) (Carballo *et al*., 2008; Cuetos *et al.,* 2010) can be used for characterising the changes of functional group in the organic matter during composting. The FT-IR spectra show the absorbance bands which represent the organic and inorganic functional groups at different frequency depending on the bond strength. Stronger bonds are generally absorbed at higher frequencies due to their great stiffness (Wade Jr., 2003). On the other hand, TGA had been used to characterise organic matter and thermal behaviour of the organic fraction processes (Ave´rous and Le Digabel, 2006). Cuetos *et al.* (2010) defined TGA as a technique based on continuous measurement of weight loss by a sample during heating in a controlled atmosphere. The techniques have yet to be applied to characterise the compost from oil palm biomass. Thus, the objective of this study is to investigate the effects of composting conditions in the biodegradation of oil palm biomass on commercial scale using FT-IR and TGA.

MATERIALS AND METHOD

The samples of raw materials (EFB and POME) and product (compost) (approximately 1 kg each) were collected from three compost plants (P1, P2 and P3) located in Sabah, Negeri Sembilan and Pahang, Malaysia respectively. A total of nine samples were collected and summarised in *Table 1*. Samples were stored at 4°C prior to analyses. The samples were manually homogenised, quartered and heated for 24 hr at 110°C for the drying process. Dried samples were manually ground in dry mill and screened through ≤ 1 mm sieve for analyses.

Fourier Transform-infrared (FT-IR) Spectroscopy

The samples were analysed using a FT-IR spectrometer (PerkinElmer Spectrum 100) equipped with universal attenuated total reflectance (UATR) accessories. The FT-IR absorbance spectra were recorded in the range of 4000 cm^{-1} to 400 cm^{-1}. The experiment was set up as described by Nithya *et al.* (2011).

Thermogravimetry Analysis (TGA)

The TGA was performed using thermal analyser, Mettler Toledo TGA/SDTA 851. The dried samples in the range of 10 mg to 20 mg were combusted from 30ºC to 800ºC at a heating rate of 10°C min^{-1} with a consistent nitrogen flow of 10 ml min^{-1}. Thermograms were recorded in terms of the percentage of weight loss of the sample whereas derivative thermogravimetry (DTG) curves were recorded as the rate of weight loss.

RESULTS AND DISCUSSION

Table 2 showed the composting parameters at P1, P2 and P3. The three plants employed an open windrow composting system. The compost piles were covered to avoid contact with rain which can affect the moisture content of the piles. From *Table 2*, P1 had the shortest composting period as compared to P2 and P3. The P2 took a longer composting period due to the use of untreated EFB while P3 did not have additional microbes for composting. The use of shredded EFB combined with additional microbes in composting enhanced the efficiency of the process. Further chemical changes were observed and discussed using FT-IR spectra and TGA.

Fourier Transform-infrared (FT-IR) Analysis

The absorbance bands of EFB, POME and compost are shown in *Figures 1* to *3*. Interpretation of the spectra was based on the studies listed in

TABLE 1. SUMMARY OF SAMPLES COLLECTED FROM COMPOST PLANTS

Description	Plant 1 (P1)	Plant 2 (P2)	Plant 3 (P3)
Empty fruit bunches (EFB)	P1(EFB)	P2(EFB)	P3(EFB)
Palm oil mill effluent (POME)	P1(POME)	P2(POME)	P3(POME)
Compost (C)	P1(C)	P2(C)	P3(C)

TABLE 2. COMPOSTING PARAMETERS AT P1, P2 AND P3

Parameters/description	Unit	Compost at Plant 1	Compost at Plant 2	Compost at Plant 3
System	-	Windrow piles under roof and concrete flooring	Windrow piles under roof and concrete flooring	Windrow piles covered with canvases
Materials	-	Shredded EFB + pre-treated POME	EFB + pre-treated POME	Shredded EFB + pre-treated POME
EFB:POME	-	1:2.6	1:2.5	1:3
Pile size (HxWxL)	m	1.5 × 3.5 × 4	2 × 3.5 × 6	1.5 x 2 x 4
Turning frequency	times/week	1 - 3	1 - 2	1 - 3
Turning machine	-	Patented windrow turner	Plougher and pulviser	Tractor
Moisture of pile	% (w/w)	50	50	50
Additional microbes	-	Yes	Yes	No
Composting duration (days)	-	20	45	50

Note: EFB - empty fruit bunch. POME - palm oil mill effluent.

TABLE 3. ABSORBANCE BANDS IN FOURIER TRANSFORM-INFRARED (FT-IR) SPECTRA RELATING TO FUNCTIONAL GROUP FROM LITERATURE SOURCES ON COMPOSTING STUDIES

Frequency (cm^{-1})	Functional group	References
3 500 - 3 310	N-H stretching vibration	Wade Jr (2003)
3 400 - 3 000	O-H stretching (vibration of carboxylic and alcoholic group)	Cuetos *et al.* (2010) Brunetti *et al.* (2012) Carballo *et al.* (2008)
2 960 - 2 850	C-H stretching of aliphatic structures	Carballo *et al.* (2008) Brunetti *et al.* (2012) Smidt *et al.* (2005; 2011) Cuetos *et al.* (2010)
1 740 - 1 700	C=O stretching carbonyl group C=O vibration of bonded conjugated ketones	Brunetti *et al.* (2012)
1 660 - 1 620	C=C vibration of aromatic carboxylates C=O stretch of primary amide lignocellulose, vibration of aromatic skeleton	Carballo *et al.* (2008) Brunetti *et al.* (2012) Smidt *et al.* (2005; 2011) Palanivell *et al.* (2012)
1 600 - 1 500	N-H deformation and C=N stretching of amides (amide II)	Carballo *et al.* (2008) Brunetti *et al.* (2012) Smidt *et al.* (2011)
1 460 - 1 430	O-H in plane band of carboxylic acids aliphatic C-H groups	Brunetti *et al.*, 2012 Carballo *et al.* (2008) Palanivell *et al.* (2012) Smidt *et al.* (2005)
1 390 - 1 320	Aromatic primary and secondary amines	Carballo *et al.* (2008) Smidt *et al.* (2005)
1 260 - 1 230	C-O stretch of carboxylic acid C-N stretch of amide	Palanivell *et al.* (2012) Brunetti *et al.* (2012) Smidt *et al.* (2005; 2011)
1 080 - 1 020	C-O stretching of polysaccharide components	Brunetti *et al.* (2012)

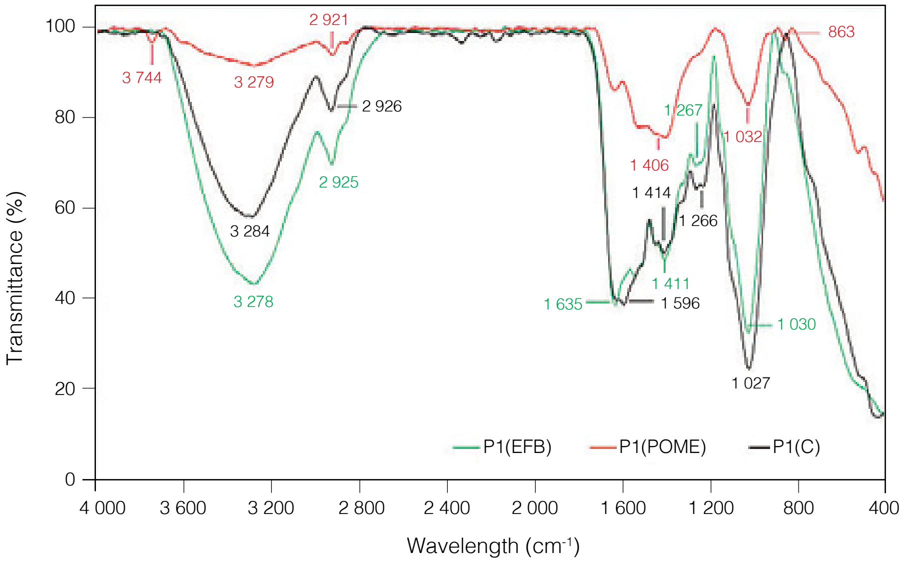

Figure 1. Fourier transform-infrared (FT-IR) spectra of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P1.

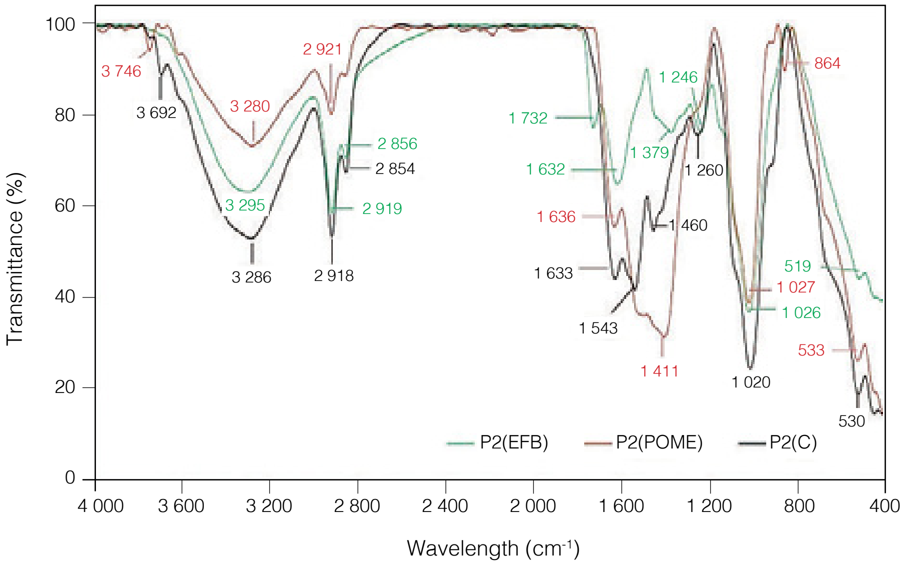

Figure 2. Fourier transform-infrared (FT-IR) spectra of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P2.

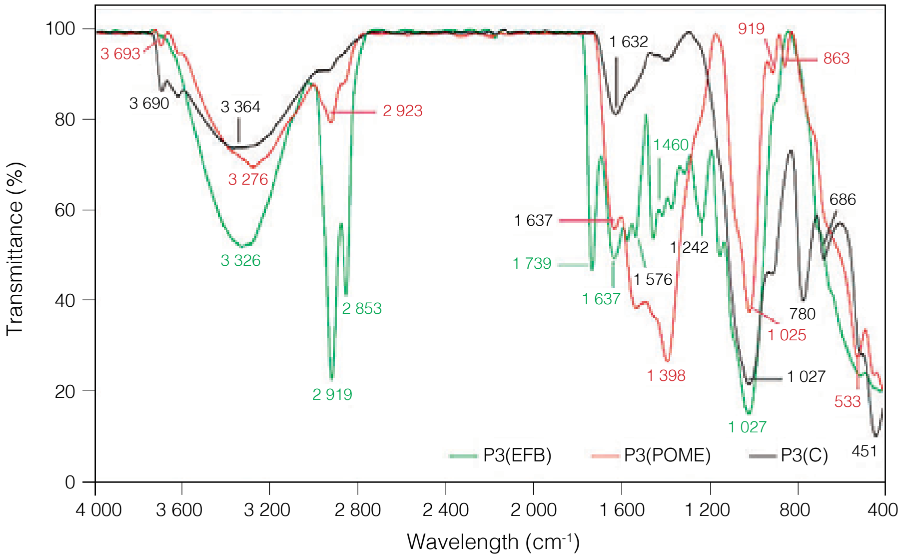

Figure 3. Fourier transform-infrared (FT-IR) spectra of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P3.

Table 3. The broad band within the range of 3370 cm^{-1} to 3270 cm^{-1} decreased for composts P1(C) and P3(C) as compared to EFB for P1(EFB) and P3(EFB), respectively. This was attributed to the weakening of hydrogen bond of the carboxylic acid in the composts. For P2(C), the band was shifted slightly from 3295 cm^{-1} to 3286 cm^{-1} which indicated the weakened hydrogen bonding in the carboxylic group. The difference was due to the pre-treatment of EFB where EFB at P1 and P3 were shredded before composting while the untreated EFB was used at P2.

There were sharp spikes superimposed with the O-H band stretching absorption appearing around 3690 cm^{-1} both for P2(C) and P3(C) (*Figures 2* and *3*). A single spike indicated a secondary amine (N-H) (Wade Jr, 2003). In the present study, it was found that the source of nitrogen originated from POME as all POME samples exhibited sharp spikes appearing in the region of 3750 cm^{-1} to 3690 cm^{-1}. Nitrogen is an important element for cell growth and functioning (Tuomela *et al*., 2000). There was no N-H spikes observed around 3690 cm^{-1} for P1(C) due to the duration of composting process of only 20 days as compared to 45 days for P2 and 50 days for P3 (*Table 2*). Thus, a minimum of 45 days is the recommended period for the amine formation in compost.

The changes observed such as peak loss and band shifting to lower frequency in the range of 2930 cm^{-1} to 2915 cm^{-1} indicated the successful removal of sugar due to its utilisation as carbon source (Cuetos *et al*., 2010). Based on the FT-IR spectra, it is suggested that P2 was partially decomposed as compared to P1 and P3. The P2 used the whole EFB bunch while P1 and P3 used shredded EFB as raw material for composting. Shredded EFB consists of more exposed surface areas that can enhance the decomposition. Consequently, the changes of peak of EFB and compost at P1 and P3 were clearly observed (*Figures 1* and *3*) while for P2, the peak was shifted slightly from 2919 cm^{-1} to 2918 cm^{-1}. Thus, composting is found to be more efficient if the raw material was treated to enhance the surface area.

The major shifts from 1732 cm^{-1} and 1630 cm^{-1} for EFB to 1640 cm^{-1} and 1540 cm^{-1} for compost showed in *Figures 1* and *2* were caused by the N-H in plane band vibration. This was due to the growth of microbes and their activities (Smidt *et al.,* 2011). The band shift also suggested the transformation in part of the material from carbonyl into amide. Smidt *et al.* (2011) found the secondary amide band at around 1570 cm^{-1} to 1510 cm^{-1} was stronger and less overlapping. The enrichment in amide and aromatic structures may be explained by the carbon loss (Calderón *et al*., 2006), microbial decomposition of alcoholic and acid structures (Amir *et al*., 2005) and digestion process, where some part of carbon was emitted as biogenic carbon dioxide (Cuetos *et al*., 2010). Amide contains nitrogen and carbonyl as the main functional groups. An increase in humification may also reflect this band shift. Humification is the degradation of the organic matter into humic acids. Based on the study by Smidt and Lechner (2005), humic acids showed a strong band at 1640 cm^{-1} that appeared during the composting process. The sharp peak of P3(EFB) at 1740 cm^{-1} and 1637 cm^{-1} decreased and shifted into 1632 cm^{-1} [P3(C)], suggesting slow activity and growth of microbes at the end of the biodegradation process and the complete digestion of EFB at P3.

The bands at 1410 cm^{-1} and 1370 cm^{-1} were shifted to a higher frequency at 1414 cm^{-1} and 1460 cm^{-1} for P1 and P2, respectively (*Figures 1* and *2*). The shifting suggested the formation of a stronger bond where the vibration of aromatic skeleton became stronger. Frequency increases with bond energy and changes occur as a result of conjugation and ring strain (Wade Jr, 2003). The peaks at 1500 cm^{-1} to 1200 cm^{-1} at P3(C) disappeared and suggested the complete decomposition of EFB (*Figure 3*).

Thermogravimetry Analysis (TGA)

Figures 4 to 6 show the TGA profiles of raw materials and product from P1, P2 and P3, respectively. TGA profiles of P1 and P2 showed an almost similar trend. Two stages of weight lost were observed for P1 and P2 while P3 showed only one stage. The first stage was approximately from 60°C to 130°C indicating the loss of residual water from 5% to 25% of the total volume for all samples. The weight loss from 35% to 55% of the total volume from 220°C to 350°C suggested the loss of carbon and carbohydrate. It was due to the utilisation as carbon source for microbiological growth and activities during the composting process. Further weight loss of material combusted at 800°C and above indicated a higher residual matter. Weight loss for P3(C) was only 40% of the total volume indicating a stable and complete digestion which is in agreement with the discussed FT-IR results.

DTG profiles of raw materials and products from P1, P2 and P3 are shown in *Figures 7, 8* and *9* respectively. DTG profiles showed two clearly differentiated peaks and were well corresponded to the TGA profiles. There was one peak at the range of 50°C to 130°C and another peak between 220°C to 350°C for P1 and P2 (*Figures 7* and *8*). Carballo *et al.* (2008) found that degradation between 200°C to 350°C indicated the main losses of organic matter, due to the combustion of aliphatic structures. In this study, drastic loss of weight between 200°C to 350°C was mainly attributed to the combustion of carbohydrates in the degradation of hemicellulose. For P3(C), a weak peak was observed at 200°C to 400°C (*Figure 9*) which suggested a complete digestion during the composting process. According to Smidt and Lechner (2005), as compost became more stable, products that burned within the range

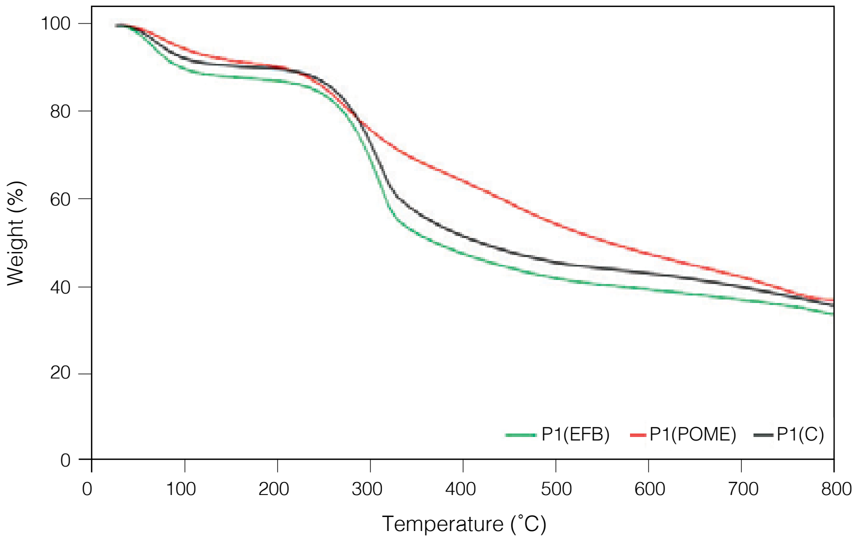

Figure 4. Thermogravimetry analyses (TGA) profile of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P1.

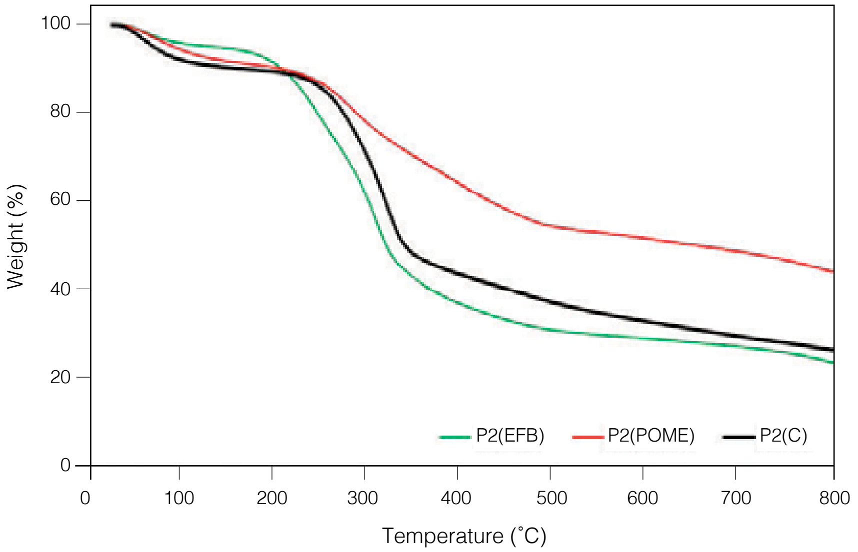

Figure 5. Thermogravimetry analyses (TGA) profile of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P2.

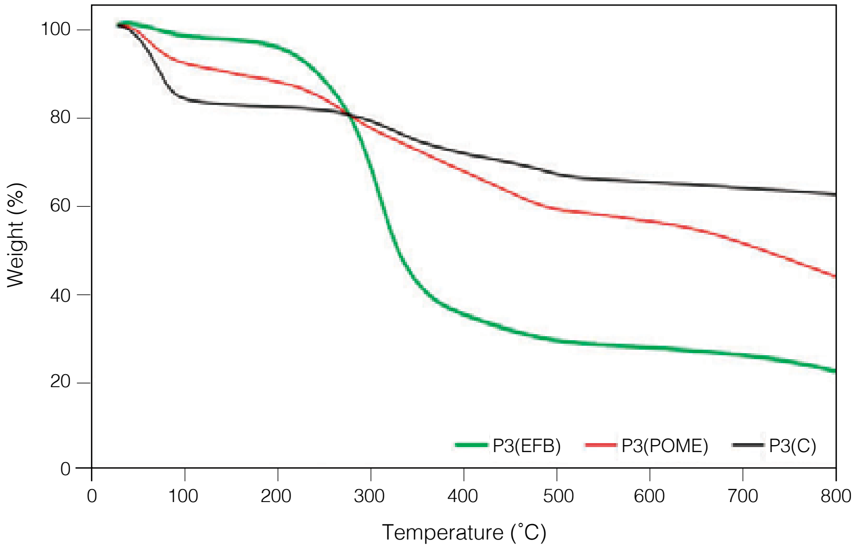

Figure 6. Thermogravimetry analyses (TGA) profile of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P3.

of temperatures 200°C to 350°C disappeared.

Comparing EFB and compost, the peaks were observed to have shifted from 315°C to 324°C for P2 and from 314°C to 331°C for P3 while no significant changes were observed for P1 at the temperature ranging from 300°C to 350°C (*Figures 7* to *9*). The P1 and P2 showed a strong peak while P3 showed a weak peak. The peaks suggested the presence of a complex material. The strong peak with greater intensity being displaced to the higher temperature range can be related to the formation of complex compounds during microbiological activity (Cuetos *et al.*, 2010). The shifting was in accordance to the increase in the aromatic structures and polysaccharides in compost as previously observed and described in FT-IR analyses. As such, the TGA

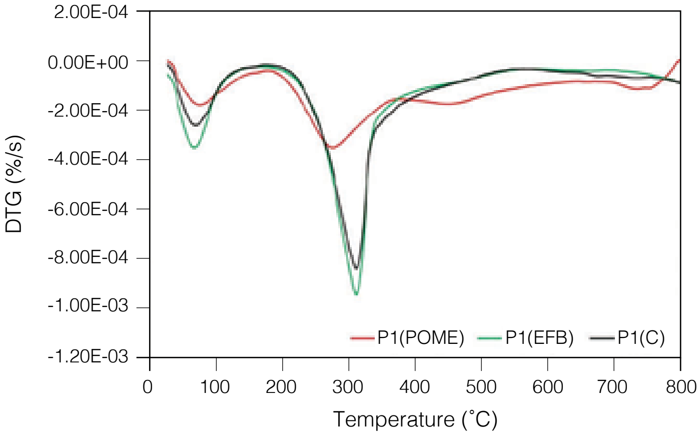

Figure 7. Derivatives thermogravimetry (DTG) profile of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P1.

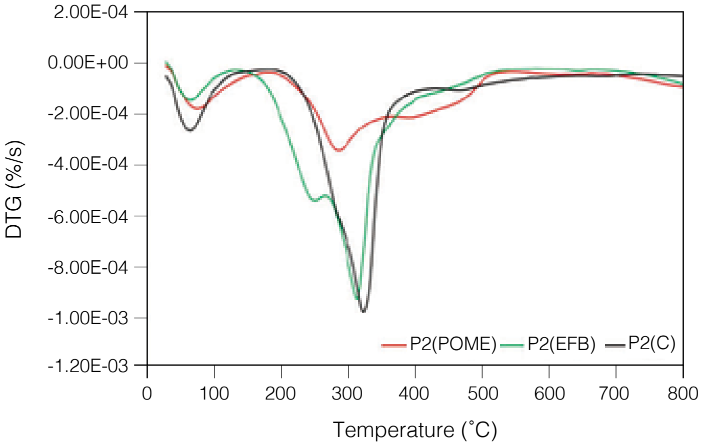

Figure 8. Derivatives thermogravimetry (DTG) profile of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P2.

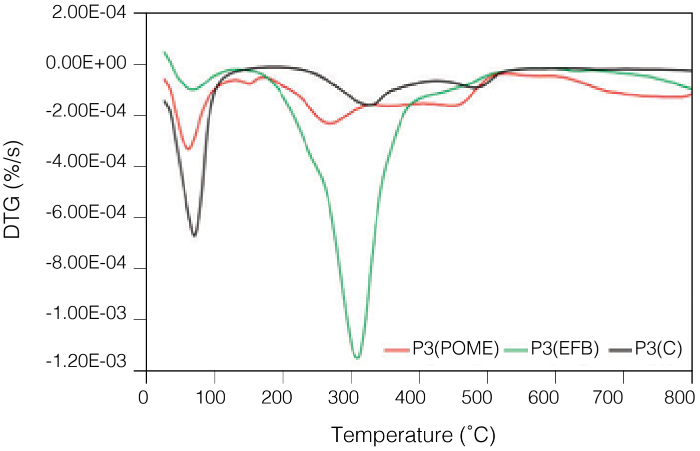

Figure 9. Derivatives thermogravimetry (DTG) profile of empty fruit bunches (EFB), palm oil mill effluent (POME) and compost (C) collected at P3.

supported the recommendation found using FT-IR that 20 days was insufficient for the generation of complex materials during composting.

From the present study, thermal degradation of EFB at lower temperature suggested that it has lower residual material due to the reaction from hydrophobic group. This was in accordance with the presence of carboxyl group at the early stage of composting. Thermal degradation for compost occurs at higher temperature due to the presence of higher residual material (hydrophiles). Higher residual material refers to a complex material consisting of carbonyl, amide and hydroxyl as the main functional groups. This reflects the stability and degradation temperature for compost. A stabilised product shows the peak of weight loss at higher temperature (Cuetos *et al*., 2010). High temperature peak suggests the thermal degradation of resistant aromatic structures and polynuclear systems of higher molecular weight (Carballo *et al*., 2008). Thus, a minimum of 45 days is the recommended period for the generation of higher residual materials for compost stability.

CONCLUSION

The study found that the composting of oil palm biomass is affected by factors including pre-treatment of raw material and the use of microbes. The most efficient process consisted of the use of shredded EFB for composting. It required 55% less amount of time as compared to untreated EFB and 60% less amount of time as compared to treatment without any microbes. The FT-IR spectra and TGA showed that composting resulted in the loss of aliphatic structures by formation of aromatic structures. This led to a stronger intramolecular bond and subsequently increasing the stability of the compost.

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