



## Fruit waste as feedstock for recovery by pyrolysis technique



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### ABSTRACT

Fruit wastes of mango endocarp and waste fruits peel from banana, orange and watermelon were pyrolysed respectively and subjected to different analyses to examine their thermal behaviour, chemical functional group, elemental and proximate content. The fruit wastes were dominated by volatile matter (52–67 wt%) containing aliphatic hydrocarbons, fatty acids and lignocellulosic components that can be recovered as potential fuel or chemical feedstock via pyrolysis. The wastes were also detected to have considerable amounts of fixed carbon (30–36 wt%), thus showing potential to be pyrolysed to produce biochar for use as activated carbon or catalyst support. The wastes can be pyrolysed at  $\geq 400$  °C to convert the majority of the waste content into volatiles for recovery as useful bio-oil and bio-gas, and the remaining solid mass can be recovered as bio-char. The results demonstrate that the fruit wastes show exceptional promise as a feedstock for pyrolysis conversion into potentially useful products.

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### 1. Introduction

Fruit is widely consumed in the world due to its nutritious contents (e.g. rich in vitamins) and variety of applications. For example, fruit can be served as a dessert after meal, processed into juices or refined into fruit jam. Consequently, a significant amount of fruit waste has been generated from these applications, particularly the fruit peel resulting from the fruit processing industries. There were 33 million tons of oranges being processed into orange juice by the food industry in 2006 and this has led to the production of 20 million tons of waste orange peels to be disposed (Aguiar et al., 2008).

At present, there are three common methods used for disposing the fruit wastes, namely: composting, landfilling, and open burning. However, none of these methods are fully practical to dispose the fruit wastes since they could contribute to various environmental issues. The release of unpleasant odour during composting would lead to poor air quality (Bu et al., 2014), while landfilling would lead to liberation of greenhouse gases (e.g. CH<sub>4</sub>) that contribute to global warming, and the possible discharge of toxic compounds such as dioxin from open burning could cause

some acute health effects such as headache, fatigue, diarrhoea, and insomnia to human being (Kimbrough and Jensen, 2012).

The fruit wastes, despite being a high-volume waste to be disposed of, also represent a renewable and sustainable resource to be exploited rather than simply disposed by landfilling and composting. Fruit wastes are mainly comprised of soluble sugars (e.g. glucose, fructose, and sucrose), cellulose, hemicellulose, and lignin that could be a suitable feedstock for bio-ethanol production. However, the production of bio-ethanol from fruit wastes is usually costly due to the need of high energy in the pre-treatment application (e.g. steam explosion) (Boluda-Aguilar et al., 2010).

Fruit wastes are also considered as biomass since they are derived from plant-based material. Pyrolysis technology has been reported to demonstrate promising performance in the transformation of biomass such as coffee hulls (Domínguez et al., 2007) and rice straws (Lin et al., 2014) into value-added products such as H<sub>2</sub> gas and bio-fuels. It has also shown to be effective in the conversion of microalgae (Hu et al., 2012) and oil palm shells (Salema and Ani, 2012) into biofuel. These biomass materials were thermally cracked and decomposed in an inert environment to produce pyrolysis products comprising of biochar, bio-oil, and also gases containing H<sub>2</sub>, syngas and light gaseous hydrocarbon. The biochar could be utilized as a catalyst or catalyst-support in tar decomposition (Shen and Yoshikawa, 2013), or used as soil amendment to increase the microbial activity and nutrient retention period in the soil that in turn improves the soil fertility (Lehmann et al., 2011).

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The bio-oil could be used as chemical feedstock or upgraded to transportation fuel depending on its compositions (Russell et al., 2012; Salema and Ani, 2011), whereas the gaseous products (e.g. H<sub>2</sub>, methane, and syngas) could be used as a fuel in the gas engine or fuel cells (Lam et al., 2010, 2016). Thus, pyrolysis could potentially be used as an alternative technique to convert fruit wastes into potentially useful materials.

This study was performed to investigate the feasibility of fruit wastes to be utilized as a feedstock for pyrolysis recovery into potentially useful products such as biochar, bio-oil, and bio-gas. This included examination of the chemical functional groups, elemental and proximate composition of the fruit wastes. The wastes were then pyrolysed via a thermogravimetric approach in order to examine their thermal degradation behaviour and the different types and stages of chemical reactions (e.g. evaporation, decomposition) that could occur during the pyrolysis treatment. Fruit wastes that are unexplored but abundant and readily available in Malaysia were selected for this study due to their ease of acquisition. There are limited studies performed on the pyrolysis recovery of fruit waste; there were only studies performed on the pyrolysis of orange peels to produce biochar as adsorbent materials for naphthalene and 1-naphthol (Chen et al., 2011) in addition to studies performed on pyrolysis conversion of orange peels into bio-oil containing benzene, toluene, and xylene (Miranda et al., 2009). Therefore, this study was performed with the aim of revealing the potential of fruit wastes as a pyrolysis feedstock, and also aims to provide useful information as to the suitable operating conditions (e.g. temperature, modes of pyrolysis) in order for optimal recovery of desirable products (e.g. bio-oil, bio-gas, bio-char) from the pyrolysis of fruit wastes.

## 2. Materials and methods

### 2.1. Sources of fruit wastes

Four types of fruit wastes were selected and characterized in this study, namely: mango endocarp and waste fruits peels from banana, orange, and watermelon. The fruit wastes were collected from local fruit stalls in Kuala Terengganu, Terengganu, Malaysia.

### 2.2. Preparation of fruit wastes

The fruit wastes were rinsed with tap water to remove dirt and sand particles. Next, the wastes were dried in an oven for 24 h at 105 °C to remove moisture content. The dried fruit wastes were cut into small pieces with a diameter of approximately 0.5–1.0 cm, and then they were stored before being subjected to characterization by chemical analysis followed by pyrolysis treatment.

### 2.3. Characterization of fruit wastes

The waste samples were analysed using a Perkin Elmer Spectrum 100 Fourier Transform Infrared (FTIR) spectrometer to identify the chemical functional groups present in the samples. A thin KBr (potassium bromide) disc method was used through which the waste sample was first mixed with KBr before subjected to FTIR analysis. The mixed sample was vigorously ground into a fine powder form in a dried mortar using a pestle. Before the infrared (IR) analysis was initiated, a background scanning was performed to exclude the peaks caused by the moisture and carbon dioxide present on the sample holder of the FTIR spectrometer. The IR analysis was then performed at wavenumber ranging from 400 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>, and 16 scans were performed for each sample. The infrared spectrum obtained was presented in a form of transmittance (%) against wavenumber (cm<sup>-1</sup>).

Elemental analysis of waste samples was conducted using a FlashEA 1112 CHNS elemental analyser to quantify the carbon, hydrogen, nitrogen and sulphur contents in the sample, whereas the oxygen content was determined by mass difference (Liu and Han, 2015). The fruit wastes were dried in an oven at 105 °C to remove any residual moisture content. Next, the fruit wastes were combusted with oxygen at 1000 °C to produce CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, and SO<sub>2</sub> as products of combustion. These products were then transferred through the system by Helium (He) as the carrier gas. The contents of carbon, hydrogen, and sulphur were detected quantitatively by the selective IR absorption detectors whereas the content of nitrogen was measured by a thermal conductivity detector. The results obtained were presented in weight percent (wt%).

### 2.4. Pyrolysis of fruit wastes using TGA

The fruit wastes were pyrolysed to examine their thermal degradation behaviour under an inert environment using a Mettler Toledo Thermogravimetric Analyser coupled with a gas controller. An approximately 10 mg of waste sample was measured and inserted onto a 20 µL alumina crucible. The crucible containing the waste samples was then placed in a thermobalance. The waste samples were heated and pyrolysed in an inert N<sub>2</sub> atmosphere from ambient temperature to 900 °C at a heating rate of 10 °C/min and a gas flow rate of 25 ml/min. The results were presented as TGA-DTG curves in a form of weight percent (%) against temperature in degree Celsius (°C). The TGA curves obtained from these pyrolysis experiments were used to estimate the minimum temperature required in order for pyrolysis conversion of the majority of the content of fruit wastes to occur. In addition, it allows the prediction of the different types and stages of chemical reactions (e.g. evaporation, decomposition, carbonization) occurring during the pyrolysis process.

The TGA curves were also used to determine the proximate content of moisture and volatile matter of the waste samples. The moisture content was determined by the weight loss of the sample at 110 °C while the volatile matter was determined by the weight loss observed in the ranges of temperature between 150 until 600 °C, whereas the ash content was determined by combustion of the fruit wastes in a muffle furnace at 950 °C with a holding time of 10 min. The fixed carbon content was estimated by subtracting the contents of volatile matter and ash from the original dry mass of the sample (Azua et al., 2013).

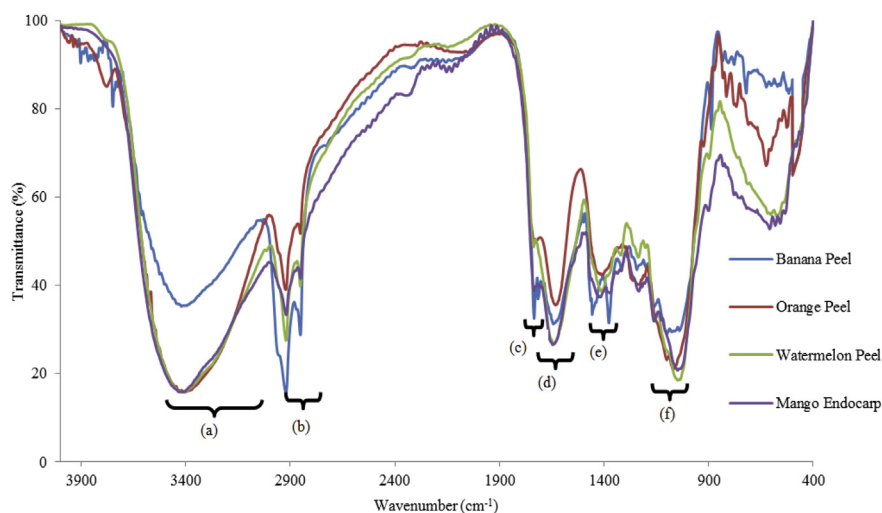
## 3. Results and discussions

### 3.1. Chemical functional groups of fruit wastes

The infrared spectra (IR) of fruit wastes obtained by FTIR analysis are shown in Fig. 1. The classification of chemical compounds present in the wastes can be derived from the functional groups that were detected as vibrational modes (or transmittance peaks) observed at different ranges of wavenumber shown in the FTIR spectra, and the results are presented in Table 1.

As shown in Fig. 1, the fruit wastes tested in this study (i.e. banana peel, orange peel, watermelon peel, and mango endocarp) have demonstrated a nearly identical pattern of IR spectra except with a small difference in the intensities of the transmittance peak detected at the different ranges of wavenumber. The nearly identical pattern of IR spectra indicates that the fruit wastes shared the similar functional groups.

The broad peak detected at 3000–3500 cm<sup>-1</sup> (i.e. peak (a) in Fig. 1) is a typical transmittance peak for O–H stretching that indicates the presence of alcohol, phenol and carboxylic acids, suggesting that these compounds are abundantly present in the fruit



**Fig. 1.** FTIR spectrum of fruit wastes. Six major transmittance peaks were detected at different ranges of wavenumber ( $\text{cm}^{-1}$ ), and they are denoted as (a) to (f), where (a): 3000–3500  $\text{cm}^{-1}$ , (b): 2800–3000  $\text{cm}^{-1}$ , (c): 1700–1750  $\text{cm}^{-1}$ , (d): 1600–1700  $\text{cm}^{-1}$ , (e): 1300–1500  $\text{cm}^{-1}$ , and (f): 1000–1200  $\text{cm}^{-1}$ .

**Table 1**

Functional groups and the classification of compounds detected in fruit wastes by FTIR analysis.

Transmittance peaks indicated by the range of wavenumber ( $\text{cm}^{-1}$ )	Wavenumber of fruit wastes ( $\text{cm}^{-1}$ ) <sup>a</sup>				Functional groups	Classification of compounds
	BP <sup>b</sup>	OP <sup>c</sup>	WP <sup>d</sup>	ME <sup>e</sup>		
(a) 3000–3500	3394	3403	3413	3414	O–H Stretching	Alcohol, phenol or carboxylic acid
(b) 2800–3000	2920, 2851	2922, 2852	2920, 2851	2919, 2851	C–H Stretching	Alkanes
(c) 1700–1750	1734	1734	1735	1735	C=O Stretching	Aldehyde, ketone or carboxylic acid
(d) 1600–1700	1633	1632	1642	1647	C=C Stretching	Alkenes
(e) 1300–1500	1457, 1377	1412	1415	1423	C–H Bending	Alkanes
(f) 1000–1200	1099	1068	1038	1048	C–O Bending	Alcohol, ether or carboxylic acid

<sup>a</sup> The values shown are the peak value detected within the particular range of wavenumber.

<sup>b</sup> BP: banana peel.

<sup>c</sup> OP: orange peel.

<sup>d</sup> WP: watermelon peel.

<sup>e</sup> ME: mango endocarp.

wastes. The broad peak is possibly due to the presence of alcohol-related functional group ( $-\text{CH}_2\text{OH}-$ ) derived from the cellulose component in the biomass (Wu et al., 2013). Fruit wastes being a biomass material that contains cellulose component could be pyrolysed to produce hydrogen as has been reported by a study performed on pyrolysis of cellulose, hemicellulose and lignin by Wu et al. (2013) (Wu et al., 2013). In addition, biomass materials generally contain natural organic compounds formed by fatty acids. Thus, it is thought that the carboxylic acids derived from the peak of O–H stretching are likely to be accounted by the fatty acid compounds present in the fruit wastes. The presence of fatty acid compounds, being the main components that can be converted into a biofuel, shows the potential of the fruit wastes to be used as a feedstock for conversion into biofuel. In particular, a pyrolysis process could be used to convert the fatty acid components in the fruit waste to produce biofuel.

The banana peel was found to show a smaller transmittance peak for O–H stretching compared to that shown by other fruit wastes, indicating that banana peel contained less compounds with O–H stretching. This corroborates with the results obtained for the elemental content of the fruit wastes (see Table 2) from which the banana peel showed the lowest content of oxygen (46 wt%) compared to the other fruit wastes ( $\geq 51$  wt%).

The sharp transmittance peak detected at 2800–3000  $\text{cm}^{-1}$  (peak (b) in Fig. 1) can be ascribed to compounds containing C–H

**Table 2**

Elemental composition (wt%) of fruit wastes.

Sample	C	H	N	O <sup>a</sup>	S <sup>b</sup>	H/C	O/C	(N + O)/C
Banana peel	47.5	6.0	1.0	45.5	0	1.5	0.7	0.7
Orange peel	42.4	5.8	0.6	51.2	0	1.6	0.9	0.9
Watermelon peel	34.0	5.1	2.9	58.0	0	1.8	1.3	1.4
Mango endocarp	41.3	5.7	0.3	52.7	0	1.6	1.0	1.0

<sup>a</sup> Determined by difference (Liu and Han, 2015).

<sup>b</sup> Not detected.

stretching with hybridisation of  $sp^3$ . In particular, it was observed that the transmittance peaks for C–H stretching were detected at around 2920  $\text{cm}^{-1}$  and 2851  $\text{cm}^{-1}$ . The transmittance peak detected at around 2920  $\text{cm}^{-1}$  refers to compounds with ‘asymmetric’ C–H stretching of the methylene group ( $-\text{CH}_2-$ ) of an alkane compound, whereas the peak at around 2851  $\text{cm}^{-1}$  refers to compounds with ‘symmetric’ C–H stretching of the methylene group of an alkane compound. The detection of transmittance peak within a range close to these wavenumbers is a strong indicator of the presence of alkanes in the fruit wastes. It was revealed that the banana peel shows high peak intensity at these wavenumbers (Fig. 1), thus indicating high alkane content. The banana peel also showed the largest transmittance peak (Fig. 1) for C–H stretching compared to that shown by other fruit wastes, suggesting that

alkanes are present in higher quantities in the banana peel. In contrast, a low content of alkanes was observed in orange peel as shown by the smallest transmittance peak of C–H stretching (Fig. 1).

The transmittance peak shown at  $1700\text{--}1750\text{ cm}^{-1}$  (peak (c) in Fig. 1) can be assigned to the C=O stretching of carbonyl compounds such as aldehyde, ketone or carboxylic acids. In addition, this transmittance peak is also an indicator of the presence of hemicellulose compound in which the C=O is likely to originate from the methyl ester ( $\text{CH}_3\text{--COO}$ ) fragment of the hemicellulose compound. The banana peel showed the highest transmittance peak in this wavenumber region, indicating that more hemicellulose compounds containing methyl ester fragment are present in banana peel compared to other fruit wastes (i.e. orange peel, watermelon peel, mango endocarp). The methyl ester fragment is also a typical chemical group that is normally found in carboxylic compounds formed by fatty acid methyl ester compounds (the key component of biofuel). This suggests that the carboxylic acids detected from the peak of C=O stretching contained fatty acid methyl ester compounds, which is favourable since the fatty acid methyl ester compounds could be converted and recovered for use as biofuel products.

For the transmittance peak observed at  $1600\text{--}1700\text{ cm}^{-1}$  (peak (d) in Fig. 1), it is assigned to compounds with the functional group of C=C stretching such as alkene compounds, which were likely to derive from the unsaturated fatty acids present in the fruit wastes. The detection of transmittance peak within the range of  $1300\text{--}1500\text{ cm}^{-1}$  (peak (e) in Fig. 1) also indicates the presence of alkanes in the fruit wastes. Combined with the results showing high peak intensity for C–H stretching at  $2800\text{--}3000\text{ cm}^{-1}$  (peak (b) in Fig. 1), this reveals that there is an abundance of alkanes present in the fruit wastes. As shown from the transmittance peak observed at  $1300\text{--}1500\text{ cm}^{-1}$  (i.e. peak (e) in Fig. 1), there was a pair of transmittance peak ( $1457\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$ ) detected for the banana peel. The transmittance peak detected at  $1457\text{ cm}^{-1}$  shows the presence of the methylene group ( $\text{--CH}_2\text{--}$ ) of an alkane compound, whereas the peak detected at  $1377\text{ cm}^{-1}$  refers to alkane compounds containing the methyl group ( $\text{--CH}_3$ ). This indicates that the banana peel contained alkanes formed by both the  $\text{--CH}_2\text{--}$  and  $\text{--CH}_3$  group. In contrast, only one transmittance peak that indicates the presence of  $\text{--CH}_2\text{--}$  group was detected for the orange peel, watermelon peel, and mango endocarp ( $1412\text{ cm}^{-1}$ ,  $1415\text{ cm}^{-1}$ ,  $1423\text{ cm}^{-1}$ , respectively), indicating the presence of

alkanes with only  $\text{--CH}_2\text{--}$  group in these fruit wastes. The presence of both alkenes and alkanes represents a potentially high-value resource for conversion into a fuel source.

It was also found that the orange peel, watermelon peel and mango endocarp show relatively higher transmittance peak for C–O bending (peak (f) in Fig. 1) at  $1068\text{ cm}^{-1}$ ,  $1038\text{ cm}^{-1}$ , and  $1048\text{ cm}^{-1}$ , respectively. The detection of the peaks for C–O bending indicates the presence of alcohol, ether, or carboxylic acids. It is thought that the peak was also derived mainly from the alcohol-related functional group ( $\text{--CH}_2\text{OH--}$ ) present as a component of the cellulose compounds present in the fruit wastes (Wu et al., 2013). These cellulose compounds could potentially be transformed into hydrogen for use as chemical feedstock (Wu et al., 2013).

Overall, the results from FTIR analysis show that the fruit waste are dominated by oxygenated compounds (alcohol, phenol, carboxylic acids, ether) and aliphatic hydrocarbons (alkanes, alkenes), and smaller amounts of aldehydes and ketones. Moreover, compounds such as cellulose, hemicellulose and fatty acids could be inferred from the detection of the functional groups present in the fruit wastes. In particular, the banana peel with a high alkane and hemicellulose contents shows potential to be converted into fuel products, and the high cellulose content shown by the orange peel, watermelon peel, and mango endocarp suggests that these wastes could potentially be transformed into hydrogen gas for use as a chemical feedstock or 2nd generation fuel.

### 3.2. Elemental content of fruit wastes

Table 2 shows the results from elemental analysis of the fruit wastes, and the distribution of these elements in the wastes is presented in Fig. 2. The results demonstrate that carbon and oxygen represented the major elements present in the fruit wastes, whereas hydrogen and nitrogen were detected in low concentration. Sulphur was not detected in the fruit wastes, probably due to the presence of a very low sulphur content that was well below the detection limit of the CHNS analyser. It was revealed that the watermelon peel shows the lowest content of carbon (34 wt%) and highest contents of nitrogen and oxygen (2.9 wt% and 58 wt%, respectively). The high content of nitrogen was likely to be derived from pyrazole alkaloids (a natural product containing nitrogen) that is commonly found in watermelon (Kikuchi et al., 2015), whereas the high content of oxygen can be attributed to the high

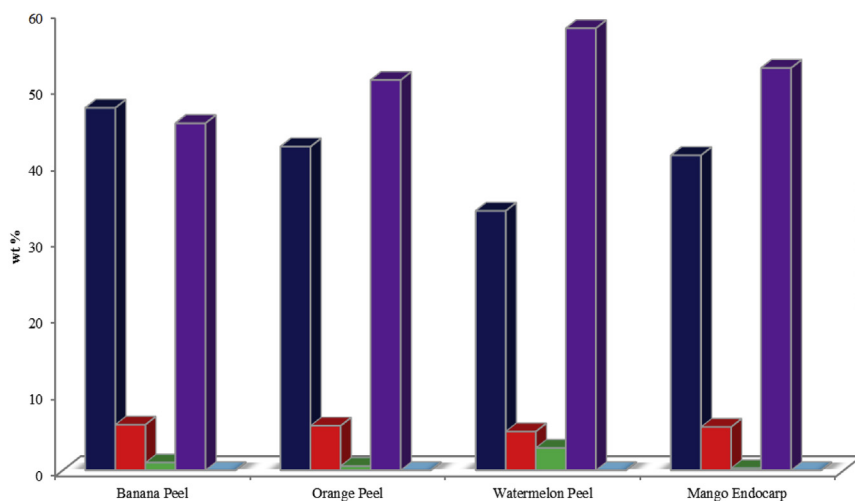


Fig. 2. Distribution of carbon, hydrogen, nitrogen, and oxygen elements in the fruit wastes. Sulphur content is not detectable by the minimum detection limit of the CHNS analyser ( $<0.05\text{ wt}\%$ ), and thus it is assumed to be  $0\text{ wt}\%$  in calculation.

amounts of oxygen-containing compounds (e.g. alcohol, carboxylic acid) present in the watermelon peel. This concurs with the findings from FTIR analysis that indicated the abundance of oxygenated compounds (e.g. alcohol, phenol, carboxylic acids) detected in watermelon peel as indicated by the large transmittance peaks detected for O–H stretching and C–O bending (peak (a) and (f) in Fig. 1).

The fruit wastes show considerable high contents of carbon (34–48 wt%), suggesting that these wastes could potentially be treated and recovered as carbon-dense material such as biochar. There are technologies that could be used to transform such biomass materials into biochar, such as slow pyrolysis (González et al., 2013), hydrothermal carbonization (Kruse et al., 2013), and gasification (Meyer et al., 2011). The biochar product could then be used as a catalyst or catalyst-support in tar decomposition (Lam et al., 2015; Shen and Yoshikawa, 2013), or applied as soil amendment to improve the soil fertility (Lehmann et al., 2011).

It was also found that the fruit wastes are highly oxygenated biomass materials containing up to 58 wt% of oxygen content, and this can be attributed to the major oxygenated organic constituents present in biomass materials, namely the lignocellulosic contents comprising of cellulose, hemicellulose, and lignin. This result is consistent with the findings from the FTIR spectrum of the fruit wastes (Fig. 1) that indicates the abundant presence of oxygen-containing compounds such as aldehyde, alcohol, ethers, carboxylic acid, ketone, and phenol.

The H/C atomic ratio can be an indicator of the existence of hydrocarbons in a substance, and the variations in the ratio indicate the different levels of saturation in the carbon–carbon bonds and in turn gives information as to the types of hydrocarbon (e.g. aliphatic, aromatic) present in the substance. The fruit wastes show a H/C ratio of approximately 2 (i.e. H/C ratio  $\geq 1.5$ ; Table 2), indicating the presence of aliphatic hydrocarbons (e.g.  $C_nH_{2n+2}$  or  $2n$ ) such as alkanes and alkenes in the wastes.

H/C ratio can also give information as to the types of chemical bonding present in the fruit wastes (Lehmann et al., 2011). Based on the H/C ratio of the waste materials that ranged from 1.5 to 1.8, which can be assumed to be within the range between 1 and 2, it can be inferred that there are hydrocarbons containing both carbon single-bonds and carbon double-bonds in the waste materials; the carbon double-bonds are derived from hydrocarbons formed by double-bonded methylene group ( $-CH=CH-$ ) and thus showing a H/C ratio of 1 with one carbon atom bonded to one hydrogen atom, whereas the carbon single-bond is derived from hydrocarbons formed by single-bonded methylene group ( $-CH_2-CH_2-$ ) and in turn shows a H/C ratio of 2 with one carbon atom bonded to two hydrogen atoms. However, these waste materials with a H/C ratio of approaching 2 (i.e. H/C ratio  $\geq 1.5$ ; Table 2) also indicates the presence of higher amounts of hydrocarbons containing carbon single-bonds (e.g. hydrocarbon with straight and/or branched

hydrocarbon chain such as alkanes that shows a higher H/C ratio) compared to hydrocarbons containing carbon double-bonds (e.g. alkenes and aromatics that normally shows a lower H/C ratio). It is thought that these hydrocarbons were derived from organic compounds (e.g. polymeric  $CH_2$ , fatty acid) naturally present in the original fruit. The presence of these hydrocarbons, particularly the alkanes and alkenes, suggests that the fruit wastes could be pyrolysed to convert the hydrocarbons into light hydrocarbons for potential use as a fuel or chemical feedstock.

The O/C atomic ratio can be related to the surface hydrophilicity nature of a substance. The fruit wastes show an O/C ratio close to 1 (Table 2), indicating the presence of compounds with one carbon atom bonded to one oxygen atom. This suggests that compounds with C–O bonding (e.g. alcohol, phenol) are likely to be present in the waste materials. Alcohol and phenol are compounds that also contain hydroxyl functional group ( $-OH$ ). The hydroxyl functional group ( $-OH$ ) of these compounds is commonly known to have a tendency to mix and bind with water molecules via hydrogen bonding. Thus, it can be inferred that if alcohol and phenol are present in the fruit wastes, these waste materials would exhibit a chemical nature of being hydrophilic (i.e. tendency to mix or dissolve in water).

The (N + O)/C atomic ratio can provide information on the polarity of the waste materials (Chen and Chen, 2009). Each atom has their own electronegativity value that measures the tendency of an atom to attract electrons from the other atom. For example, oxygen atom has higher electronegativity (3.44) than carbon atom (2.55). Hence, oxygen atom has higher tendency to attract electrons from carbon atom and this would create a net positive dipole moment from carbon atom towards oxygen atom. The bonding of carbon and oxygen atoms under this condition is said to be polar due to the existence of net positive dipole moment in between the carbon and oxygen atoms and a higher polarity would be produced if the carbon is bonded to atoms of higher electronegativity (e.g. oxygen and nitrogen atom). In contrast, the bonding in between two atoms is said to be non-polar if there is no dipole moment in between two atoms. The fruit wastes showed a (N + O)/C ratio ranging from 0.7 to 1.4 (Table 3), indicating the presence of compounds with carbon atom bonded to one nitrogen and one oxygen atom. The bonding of carbon to both nitrogen and oxygen atoms would create a net positive dipole moment from the carbon atom with lower electronegativity value (2.55) towards both oxygen and nitrogen atoms with higher electronegativity value (3.44 and 3.04, respectively). Thus, the waste materials with a higher (N + O)/C ratio are more polar than the wastes with a lower (N + O)/C ratio considering that a higher (N + O)/C ratio indicates a higher polarity resulting from the bonding of carbon atom to more nitrogen and oxygen atoms of higher electronegativity. Table 2 shows that the watermelon peel and mango endocarp have a higher (N + O)/C ratio (1.4 and 1.0, respectively) than the other fruit wastes, indicating that the

**Table 3**  
Proximate composition (wt%) of the fruit wastes.

Sample	Moisture <sup>a</sup>	Volatile matter			Fixed carbon <sup>d</sup>	Ash <sup>e</sup>
		CO <sub>2</sub> and H <sub>2</sub> O <sup>b</sup>	Hemicellulose, cellulose and lignin <sup>c</sup>	Total		
Banana peel	7	5	56	61	31	8
Orange peel	11	6	56	62	35	3
Watermelon peel	14	7	45	52	36	12
Mango endocarp	5	5	62	67	30	3

<sup>a</sup> Dry basis.

<sup>b</sup> The “H<sub>2</sub>O” is the water formed during the decomposition stage. It is different compared to the moisture content as the moisture is derived from the water originally adhered onto the surface of the fruit waste sample before it underwent decomposition reaction during the pyrolysis process.

<sup>c</sup> Volatile matter produced from pyrolytic decomposition of hemicellulose, cellulose, and lignin.

<sup>d</sup> Calculated by difference (i.e. Fixed carbon = 100 wt% – wt% of volatile matter – ash) (Azua et al., 2013).

<sup>e</sup> Obtained by combustion at 950 °C with 20 min of holding time.

watermelon peel and mango endocarp have higher polarity compared to other fruit wastes.

The surface hydrophilicity and polarity of the fruit wastes can be related to the ability to absorb water by the waste materials where hydrophilicity refers to the tendency to bind with water molecules via hydrogen bonding and polarity indicates that the wastes, being a polar substance, are more likely to be dissolved in water that acts as a polar solvent. Thus, the fruit wastes with O/C ratio close to 1, which indicates the presence of alcohol and phenol compounds with C–O bonding and hydroxyl functional group that are hydrophilic, combined with a higher (N + O)/C ratio, which indicates a higher polarity and a nature of being more likely to dissolve in water, could show higher ability to absorb water compared to the fruit wastes with a lower (N + O)/C ratio (i.e. a ratio less than 0.5). All the fruit wastes show an O/C ratio that is close to 1 (Table 2) and a (N + O)/C ratio that is both higher than 0.5 and that shown for activated carbon with both O/C and (N + O)/C ratio equalled to 0.06 (Chun et al., 2004), suggesting that the fruit wastes could show better water absorption than activated carbon as indicated by its hydrophilicity and higher polarity. Consequently, it can be inferred that if the fruit wastes are sent for disposal in landfill, their polar and hydrophilic natures would have led to the occurrence of hydrolysis process through which the larger organic molecules present in the waste materials would react with the water that are abundantly present in landfill sites and then convert into smaller molecules such as acetic acid (Molino et al., 2013). The resulting smaller molecules would then be converted by bacteria to produce methane (CH<sub>4</sub>) which would then be released as greenhouse gas into the environment to promote global warming. Thus, efforts should be made to recover the fruit wastes (e.g. acting as a feedstock for pyrolysis recovery) to divert the wastes from landfilling (with considerably long decomposition times and the risk of undesired production of greenhouse gas).

### 3.3. Proximate content of moisture, volatile matter, fixed carbon, and ash content of fruit wastes

Table 3 presents the moisture, volatile matter, fixed carbon, and ash content of the fruit wastes obtained by proximate analysis. The results showed that the fruit wastes are dominated by volatile matter (52–67 wt%) and fixed carbon (30–36 wt%) and it contained only small amounts of moisture (5–14 wt%) and ash (3–12 wt%). Watermelon peel was found to contain the highest amount of moisture (14 wt%) and this is likely due to the juicy nature of the fruit. It has been reported that fruit wastes contained a relatively high amount of volatile matter (Pinto et al., 2005), which were likely to comprise of lignocellulosic components (cellulose, hemicellulose, and lignin), chemically bonded CO<sub>2</sub>, and chemically formed H<sub>2</sub>O (see Section 3.4 for more explanation on chemically bonded CO<sub>2</sub>, and chemically formed H<sub>2</sub>O). The high content of volatile matter (up to 67 wt%) represents a favourable feature as a pyrolysis feedstock considering that pyrolysis can be performed to convert the volatile matter (representing the majority of the waste content) into useful products such as bio-oil and bio-gas that can potentially use as a fuel or chemical feedstock.

A considerable amount of fixed carbon was observed in the fruit wastes and this further indicates their potential to be recovered for use as useful carbonaceous materials (e.g. biochar) via pyrolysis. Pyrolysis has been used as a method to produce biochar from biomass materials. In the past decades, it has been reported that the biochar showed many uses such as acting as a catalyst or catalyst-support material (Shen and Yoshikawa, 2013), soil amendment (Lehmann et al., 2011), or acted as activated carbon precursor (Azargohar and Dalai, 2008). Owing to the potential use of biochar in many applications, it is thought useful to convert the fruit wastes

that contain a high content of fixed carbon into biochar by pyrolysis process.

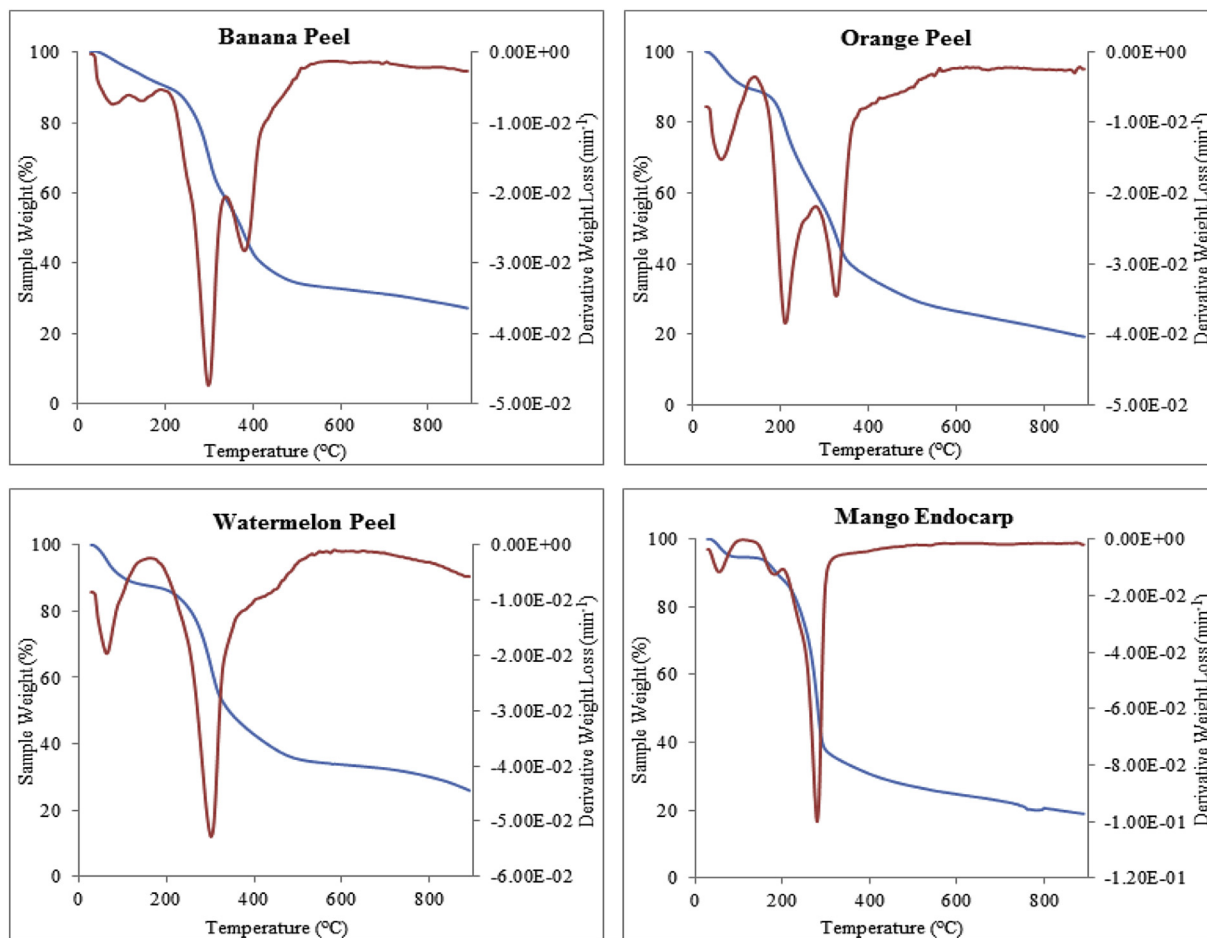
An ash content of up to 12 wt% was detected in the fruit wastes, suggesting that the waste materials should not be burned directly in boiler to produce heat energy for use in industries because ash could be produced from the burning process and in turn causes formation of fouling deposits in the boiler tube, which could lead to clogging of the boiler tube and a decrease in the boiler efficiency. However, the ash may comprise of inorganic compounds containing useful elements such as Na, K, Al, Si, and Mn that could be recovered for use as a catalyst material (Blanco et al., 2013) in the form of biochar; the presence of these inorganic compounds in biomass has been reported by other researcher in the literature (Saidur et al., 2011).

The proximate contents of the fruit wastes also provide information to assess the modes of pyrolysis (slow or fast pyrolysis) that is suitable to be used to treat and recover the fruit wastes. Slow pyrolysis is usually performed at a low heating rate (5–10 °C/min) and a long residence time (up to 24 h) whereas fast pyrolysis is conducted at a higher heating rate (up to 200 °C/min) with a short residence time (up to 30 min). It is generally agreed that slow pyrolysis represents a favourable mode of pyrolysis in producing char product while fast pyrolysis is more favourable in producing higher yields of liquid and gaseous products. The fruit wastes in this study are dominated by volatile matter (up to 67 wt%) that can be recovered as liquid and gaseous products known as bio-oil and bio-gas via pyrolysis. This indicates that fast pyrolysis can be a suitable method if optimal recovery of bio-oil and bio-gas is desired from the pyrolysis of the fruit wastes. Alternatively, slow pyrolysis can be a suitable method to convert and recover the fruit wastes as biochar since the fruit wastes also possessed a considerable amount of fixed carbon (up to 36 wt%). Overall, the results from proximate analysis indicate that the fruit wastes show potential to be converted into bio-oil and bio-gas via a fast pyrolysis approach or recovered as biochar via a slow pyrolysis approach.

### 3.4. Pyrolysis of fruit wastes

The fruit wastes were pyrolysed in an inert N<sub>2</sub> environment via TGA in order to examine their thermal degradation behaviour. Fig. 3 shows the TGA-DTG curves obtained from pyrolysis of the fruit wastes. In pyrolysis of biomass materials (e.g. fruit waste), there are several stages in which different chemical reactions could occur during the pyrolysis process, such as evaporation of moisture, devolatilization involving primary and secondary decomposition of mainly the lignocellulosic components, and possibly carbonization that results in evolution of carbon containing species such as CO<sub>x</sub>, tars, and char. The different stages and types of chemical reactions occurring during the pyrolysis of the fruit wastes can be inferred from the TGA-DTG curves obtained.

The weight of the fruit wastes was found to slightly decrease (up to 14% as indicated by the first DTG peak in Fig. 3) when the fruit wastes were initially heated to a temperature at around 100 °C, and this could be attributed to the evaporation of moisture from the waste materials. The weight of the fruit wastes dropped dramatically when the fruit wastes were heated to a temperature at between 200 and 400 °C. This dramatic fall could be attributed to the decomposition of mainly the lignocellulosic components (cellulose, hemicellulose, and lignin) of the wastes into smaller compounds (e.g. CO<sub>2</sub>); this has been reported to commonly occur in pyrolysis of biomass materials (García et al., 2013). The different trends of weight loss observed for the TGA curve of the different fruit wastes at this stage could be explained by the different compositions of the lignocellulosic components present in the fruit wastes, which underwent different rates of decomposition as a result of the different



**Fig. 3.** TGA-DTG curves of fruit wastes. TGA curve is denoted by blue line, and DTG curve is plotted with red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

chemical structure and bonding derived from the different compositions of lignocellulosic component.

It has been reported that the three main lignocellulosic components of biomass materials, i.e. cellulose, hemicellulose, and lignin, have different thermal stability and would in turn decompose at different ranges of temperature (García et al., 2013). Hemicellulose shows the lowest thermal stability and would decompose from 200 to 320 °C and this would be followed by decomposition of cellulose from 280 to 400 °C, whereas lignin being the most thermally stable compounds among the three lignocellulosic components would decompose from 320 to 450 °C. There were also studies reported that lignin would be decomposed at a higher temperature up to 1000 °C (Ferrara et al., 2014). The high temperature required to decompose lignin component could be explained by its complex compositions and structure (i.e. the highly branched three-dimensional phenolic structure). It has been reported in pyrolysis of biomass materials that the weight loss occurred between 150 and 450 °C represents the lignocellulosic components (García et al., 2013) whereas the weight loss between 450 and 600 °C represents the chemically bonded CO<sub>2</sub> and chemically formed water released from the biomass materials during the decomposition of the lignocellulosic components that occurred during the pyrolysis process (García et al., 2013). Thus, it is thought that the fruit wastes being a biomass material would possess these components and follow the similar decomposition pattern as shown by the pyrolysis of biomass materials.

The chemically bonded CO<sub>2</sub> (i.e. CO<sub>2</sub> bonded by means of

chemical bonding) was likely to be the CO<sub>2</sub> absorbed previously from the atmosphere and which was remained bonded within the cellular part of the fruit wastes. The chemically formed water (i.e. the water generated from chemical reaction) was likely to be produced from the decomposition of hemicellulose and lignin components present in the fruit wastes at high temperature (i.e. > 450 °C) (Shen et al., 2013). The formation of water molecules from decomposition of lignin has also been observed over a temperature ranging from 180 to 700 °C (Widyawati et al., 2011) where the water formation at low temperature (<450 °C) could be derived from the aliphatic OH groups of lignin while the water released at above 450 °C could be derived from the phenolic hydroxyl groups of lignin (Shen et al., 2013).

The weight of the fruit wastes experienced a steady but minimal decrease over a long range of temperature from 600 until 900 °C (Fig. 3). The small weight loss at this temperature range could mainly be attributed to the carbonization reactions (e.g. dehydrogenation, deoxygenation, condensation) that occurred during the pyrolysis process, resulting in the evolution of carbon containing species such as CO<sub>x</sub> gases, C<sub>x</sub>H<sub>y</sub> in the form of tar, and fixed carbon in the form of char. The weight loss could also be explained by the continuous decomposition of the lignin components present in the fruit wastes since it has been reported that lignin could continue to decompose at a higher temperature up to 1000 °C due to its high thermal stability (Ferrara et al., 2014).

The TGA curves obtained from the pyrolysis of fruit wastes can also be used to estimate the minimum temperature required in

**Table 4**  
Elemental and proximate compositions (wt%) of fruit wastes and other agricultural wastes.

Elemental composition	Fruit wastes (this study)	Coffee hull (Dominguez et al., 2007)	Corn straw (Li et al., 2008)	Rice straw (Huang et al., 2015)
Carbon	34–47.5	47.3	49.4	43.6
Hydrogen	5.1–6.0	6.4	5.8	5.3
Nitrogen	0.3–2.9	2.7	0.4	0.4
Sulphur	0	0.3	0.1	0
Oxygen <sup>a</sup>	45.5–58.0	37.7	44.3	50.7
<b>Proximate composition</b>				
Moisture	5–14	8	10 <sup>b</sup>	10
Volatile matter	52–67	77	87	80
Fixed carbon <sup>a</sup>	30–36	17	16	12
Ash	3–12	6	2 <sup>b</sup>	8

<sup>a</sup> Calculated by difference.

<sup>b</sup> As-received.

order for pyrolysis conversion of the majority of the content of fruit wastes to occur. This can be estimated from the temperature at which the dramatic weight loss stopped followed by the start of the curve indicating the steady pattern of small weight loss that represents the evolution of carbon containing species; this can also be estimated from the DTG curve at the temperature where a constant pattern of derivative weight loss started to be observed (Fig. 3). This temperature also represents the temperature at which most of the volatile matters are released during the pyrolysis of the fruit wastes; the volatiles released from the pyrolysis process are termed as “pyrolysis volatiles”. The pyrolysis volatiles generated, representing the majority of the waste content, could then be recovered and collected as pyrolysis products in the form of bio-oil and gases.

It can be observed from both the TGA-DTG curves in Fig. 3 that the dramatic weight loss stopped or the weight loss remained nearly constant at approximately 400 °C for mango endocarp, 520 °C for banana and watermelon peel, and 550 °C for orange peel, respectively. This indicates that most of the volatile matters in the fruit wastes were released at a temperature ranging from 400 °C to 550 °C, thus suggesting that a minimum temperature of 400 °C is required for pyrolysis conversion of the majority content of the fruit waste into pyrolysis volatiles for subsequent recovery as potentially useful pyrolysis products (bio-oil and gases). The bio-oil produced could be upgraded for use as transportation fuel or serve as valuable chemical feedstock (e.g. phenol and phenolic compounds) depending on its compositions (Du et al., 2011), while the gaseous products could be used directly in the gas engine or fuel cells, or refined into more applicable synthetic fuel via Fischer–Tropsch reaction (Lam et al., 2012). A significant amount of solid mass (up to 35 wt%) was remained after the conversion of the fruit waste into pyrolysis volatiles at this temperature, and it is present in the form of biochar due to the considerable content of fixed carbon present in the original fruit waste. The biochar could otherwise be recovered for use as a catalyst-support material or further upgraded to produce activated carbon for use as a commercial adsorbent.

Overall, the results from the pyrolysis of fruit wastes indicate that the fruit waste would undergo several stages of transformation during the pyrolysis process in which the waste materials would be subjected to chemical reactions comprising evaporation, primary devolatilisation involving decomposition of the lignocellulosic components (cellulose, hemicellulose and lignin), and carbonization over the range of temperatures considered. This resulted in the production of volatile matter representing the majority content of the fruit waste, and small amounts of moisture and water, and also considerable amounts of carbon containing species formed by gases (e.g. CO<sub>2</sub>) and char. It was revealed that a minimum temperature of 400 °C is required to recover most of the volatile matters generated from the pyrolysis of the fruit wastes. The volatile matter (i.e. pyrolysis volatiles) could then be collected as pyrolysis products in the form of bio-oil and gases for potential use as a fuel

or chemical feedstock.

### 3.5. Comparison of the elemental and proximate composition of fruit wastes with agricultural wastes

Table 4 presents the elemental and proximate compositions detected for fruit wastes in this study and that shown by agricultural wastes (i.e. coffee hull, corn straw and rice straw) reported in the literature. Oxygen (37.7–58.0 wt%) and carbon (34–49.4 wt%) represent the major elements found in both fruit and agricultural wastes. The wastes were dominated by volatile matter (52–87 wt%) and fixed carbon (12–36 wt%) followed by small amount of moisture (5–14 wt%) and ash (2–12 wt%).

Sulphur was detected in agricultural wastes such as coffee hull and corn straw, whereas no sulphur was detected for the fruit wastes. This indicates that pyrolysis of coffee hull and corn straw could produce undesirable gaseous product containing sulphur such as SO<sub>2</sub> that releases to the atmosphere. In contrast, the gaseous product produced from pyrolysis of fruit wastes would be more environmental friendly as there is no need to be concerned with the formation of sulphur-containing compounds from the fruit wastes that contain either zero or negligible content of sulphur.

The agricultural wastes were found to contain high content of volatile matter (up to 87 wt%), suggesting that pyrolysis of agricultural wastes could produce more bio-oil or biogas as the pyrolysis products based on its higher content of volatile matter. In contrast, the fruit wastes contain considerable amount of fixed carbon (up to 36 wt%), indicating that fruit wastes could otherwise be selectively converted into biochar by pyrolysis. Hence, a different set of process conditions (e.g. temperature, modes of pyrolysis) is required to pyrolyse and convert the fruit wastes into biochar compared to the pyrolysis conversion of agricultural wastes into bio-oil or biogas.

## 4. Conclusion

The results show that the fruit wastes can be a suitable feedstock for pyrolysis conversion into bio-oil, bio-gas, and bio-char for further use as potentially useful products such as fuel, chemical feedstock, or catalyst support. The fruit wastes can be pyrolysed at  $\geq 400$  °C to convert the majority of the waste content into pyrolysis volatiles for recovery as useful bio-oil and bio-gas, and the remaining solid mass can be recovered as bio-char. Fast pyrolysis can be used for optimal recovery of bio-oil and bio-gas whereas slow pyrolysis is favourable in producing biochar from the fruit wastes. To sum up, fruit wastes are highly recommended as the feedstock for pyrolysis recovery instead of being disposed by conventional yet increasingly impracticable approaches such as land-filling and open burning.



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