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THERMAL DECOMPOSITION OF TURMERIC MICROPARTICLES UNDER ATMOSPHERE CONDITION

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Abstract

The objective of this study was to evaluate thermal decomposition of turmeric microparticles under atmospheric condition. Turmeric microparticles were prepared by drying and milling Indonesian local turmeric (*Curcuma Longa*). To obtain micron size of turmeric, combination of saw- and ball-milling processes were used. The analysis was conducted by heating the prepared turmeric micropowder into the electrical heating furnace at a specific temperature. Experimental results showed that turmeric was stable at temperature of less than 100^{o} C. It begun for the decomposition process at higher temperature. Seven steps for the thermal decomposition processes were obtained. The steps involved the decomposition of turmeric into smaller molecular compounds, including curcumin, trans-6-(4,-hydroxy-3,-methoxyphenyl)-2,4-dioxo-5-hexenal; vanillin and vanillic acid; ferulic acid; and carbon. The benefit obtained in this result will give better understanding for the use of heat treatment in the turmeric and curcumin-related materials for food, drugs, and medical related uses.

Keywords: Ball-milling process, Carbon, Saw-milling process, Thermal analysis, Turmeric.

1. Introduction

Turmeric is one of the most popular organic compounds that can be found as a natural pigment (as an orange-yellow color). This material is usually utilized as a natural colouring agent in industries [1]. And, turmeric has been used mainly in Asian food [2]. Turmeric has been used due to it impart color, flavour, and aroma [3]. Interestingly, although the basic color of turmeric is yellow, as a color additive, turmeric has been used by changing its concentration in solution (see Fig. 1). Turmeric also has advantages in the chemical compounds inside it (see Table 1), specifically chemical compounds that have anti-oxidant activity [4]. This makes turmeric is studied intensively [5].

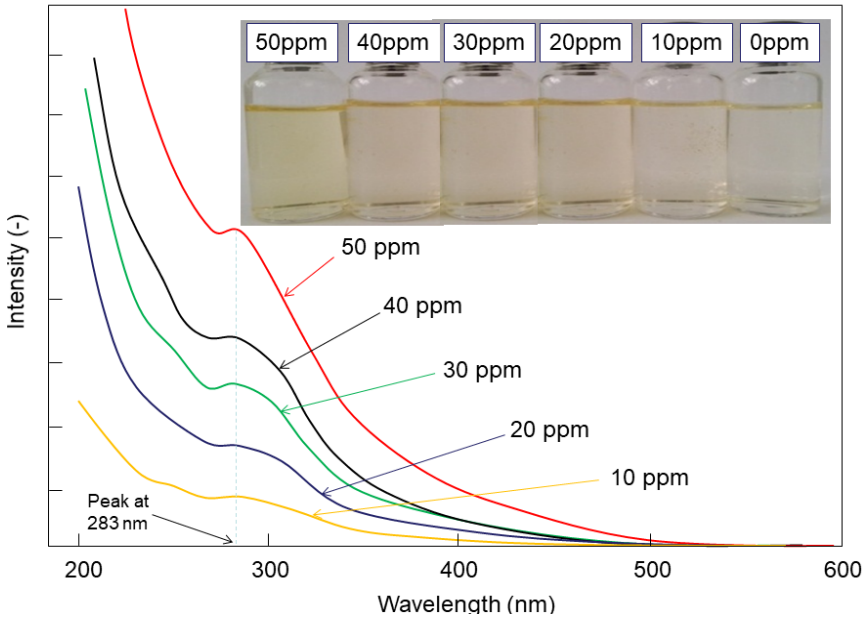

Fig. 1. Color analysis of the curcumin as a function of concentration (Figure was adopted from reference [6]).

Table 1. Chemical compound inside the turmeric (Table was adopted from reference [3]).

No.	Chemical compound	Amount (%)
1	α-Pinene	1.10
2	Myrcene	0.69
3	α-Phellandrene	20.42
4	α-Terpinene	1.26
5	p-Cymene	3.61
6	1,8-Cineole	10.30
7	3-Carene	0.35
8	γ-Terpinene	1.01
9	Terpinolene	6.19
10	α,cis-Bergamotene	0.19
11	β,cis-Farnesene	0.36
12	α-Humulene	0.23

13	γ-Curcumene	0.70
14	α-Curcumene	2.90
15	Zingiberene	6.90
16	β-Bisabolene	1.23
17	cis,γ-Bisabolene	0.37
18	β-Curcumene	0.51
19	β-Sesquiphellandrene	5.45
20	Ar–Turmerol	0.93
21	α-Turmerone	19.8
22	β-Turmerone	7.35
23	Ar–Turmerone	1.08
24	Monoterpene hydrocarbons	34.6
25	Monoterpenes oxygenated	10.30
26	Ethers	10.30
27	Sesquit hydrocarbons	18.80
28	Sesquit oxygenated	29.20
29	Water	7.10
	Total	100.00

Our previous studies have reported the utilization and the extraction of curcumin from turmeric [1, 6,9-13]. However, we did not report in detail about what phenomena during the thermal analysis of turmeric. As a continuation of previous reports, the purpose of the present study was to investigate the thermal decomposition profile of turmeric microparticles under atmospheric condition. Different from other reports that use directly the turmeric [7], the present study used turmeric powder with sizes of micrometer range. Micrometer-sized turmeric was used in this study to against problems in the heat penetration and distribution. Different from bulk turmeric, heat in the micron size particle can be transferred and penetrated to the deepest position, leading to the homogenous heat distribution in the material. However, in some cases, nanoparticles are the best since the quantum effects in the nanoparticles somewhat can disturb the heat impact analysis. Micrometer-sized turmeric has shown to have identical chemical properties with its bulk part [12] that makes the heat analysis using this type of material is no longer a problem.

To get micrometer-sized turmeric powder, fresh Indonesian local turmeric was dried, saw-milled, and ball-milled. In this study, analysis was conducted by heating the prepared turmeric powder at specific temperature, ranging from room to 600^{o} C. To support the analysis, electron microscope, thermal gravity analysis, and Fourier transform electron microscope were used. Understanding the properties of turmeric (specifically thermal decomposition) will give information on how to treat and use turmeric in the realistic applications.

2. Method

Turmeric (*curcuma longa L.*) used in this study was obtained and purchased from a local market in Bandung, Indonesia, in which the supplier for turmeric is from turmeric farm in Bandung, Indonesia. To produce turmeric microparticles, the purchased turmeric was washed, sliced, cut into sizes of 5-10 mm, dried at 50°C overnight, re-heated at 100°C for 4 hours, and milled (using two steps of milling procedures).

In the milling procedure, the process was used two types of milling processes: saw-milling and ball-milling processes. All the milling processes were done in the batch-typed milling apparatus to ensure that there is no in and out of heat and materials during the milling process. All milling processes was conducted in room temperature to ensure there is no involvement of heat during the milling process for reducing the size. Detailed information regarding the equipment used in the saw-milling and ball-milling processes are described in our previous studies [12, 13].

In the saw-milling process, we used a milling reactor vial (*i.e.*, Teflon cylinder with a specific inner dimension (height = 10 cm and diameter = 7 cm) equipped with four 3-cm jigsaw blades. The milling process was done at a specific condition (18,000 rpm; 5 minutes).

Regarding the ball-milling processing step, the apparatus for milling was a milling vial (*i.e.*, stainless steel cylinder vial with a specific inner dimension (length = 14 cm and diameter = 7 cm)) and 8-mm stainless steel balls. The process was done for 30 minutes with a rotation speed of 100 rpm. To get optimum condition, the mass ratio of ball and turmeric sample was fixed at a specific value (100:1). The working volume was fixed at 30% to ensure the ball-milling process to get micrometer-sized particles.

In a typical procedure, 50 mg of turmeric microparticles was put into the electrical furnace under atmospheric condition at the specific temperature. The heating rate was 50° C/min. Then, when the temperature reach a specific temperature, the heating process was hold for 10 min. To obtain the effect of temperature on the turmeric properties precisely, the temperature was fixed between 25 and 600^{o} C. The heated material was cooled to room temperature (a cooling rate of 50^{o} C/min). To analyse the physicochemical properties of the sample, several characterizations were utilized: Thermal Gravimetry (TG) and Differential Thermal Analysis (DTA) (DTG-60A, Shimadzu Corp., Japan; heating rate = 5^{o} C/min; flow of air = 200 mL/min; for analysing temperature profile) and Fourier Transform Infrared Spectroscopy (FTIR, FTIR-4600, Jasco Corp., Japan; for analysing the chemical bonding).

3. Result and Discussion

Figure 2 presents the SEM images of turmeric powder after saw and ball milling. As shown in Fig. 2(a), adding the saw-milling processing step to the dried turmeric allows the obtainment of powder products with a mean size of about 66 micrometers. Some particles were also obtained with sizes of several micrometers (Fig. 2(b)). The shape of saw-milled particles is sharp edge. Then, some of the products have needle shapes (Fig. 2b). The successful size-reduction process in changing their sizes from their originated form was gained (Fig. 2(c)). However, the sizes were limited to the dozens micrometers only and the size distribution is still broad. By additional ball-milling process after the saw milling, the more size-reduction process can be obtained (Fig. 2(d)). High magnification of SEM image showed the particles with blunt edge (Fig. 2(e)). The size of particles decreased down to about 8 micrometers with narrow particle size distribution (Fig. 2(f)), confirming that the combination of saw- and ball-milling processes is effective to create micrometer-sized turmeric particles.

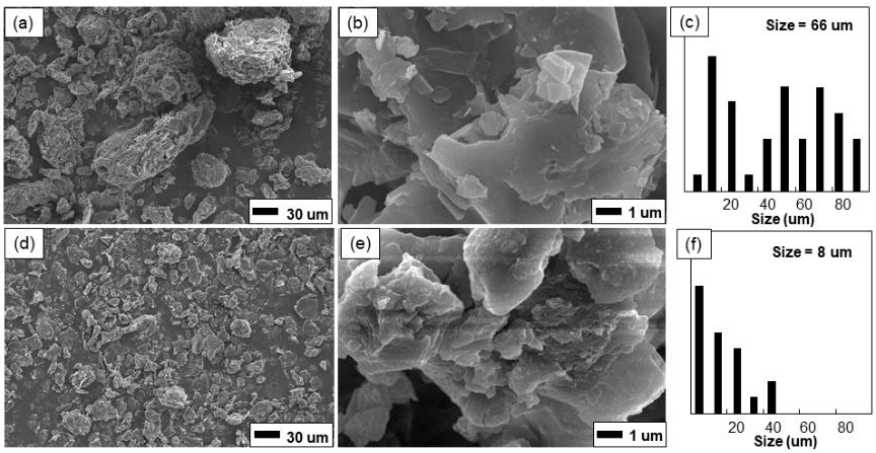

Fig. 2. The SEM images of the turmeric after additional saw-milling and ball-milling processes.

Figures 2(a) and (b) are samples prepared by saw-milling process. Figures 2(d) and (e) are the SEM analysis images of turmeric sample produced using the saw-milling and the ball-milling processes, respectively. Figures 2(b) and (e) are the high-magnified SEM images of Figs. 2(a) and (d), respectively. Figures 2(c) and (f) are the size distribution analysis of the samples shown in Figs. 2(a) and (d), respectively.

Figure 3 shows the analysis of thermal decomposition of turmeric using the TG-DTA apparatus. The loss in masses begins at temperature of about 60°C and ends at about 500°C. The mass after heated at 100°C was more than 95%, in which this is in a good relationship with the analysis results of water content in the turmeric as shown in chemical compound in Table 1. Further increasing temperature resulted the several steps of mass degradations, and each step occurred in the specific temperature (presented in vertical dashed line in Fig. 3). This is due to different thermal characteristics and reactions (see panelled image in right-top in Fig. 3). The final mass after heated 500°C is about 20%. The sample heated at this temperature was a black powder, in which this indicates the complete decomposition of turmeric into carbon. Detailed stages are:

- The stage I (begins at about 60°C and ends at about 100°C). The weight loss was less than 5%. This mass degradation is from the removal physically adsorbed water in the turmeric sample [14];
- The stage II (begins at about 100°C and ends at about 120°C) (route R1). The weight loss was about 15%. The main reason is due to the degradation of curcumin component into trans-6-(4, -hydroxy-3, -methoxyphenyl)-2,4-dioxo-5-hexenal [1];
- The stage III (route R2), in which the weight loss is 15%, started at about 120°C and ended at about 150°C. This is because of the decomposition of 6-(4, -hydroxy-3, -methoxyphenyl)-2,4-dioxo-5-hexenal become ferulic acid [1];
- The stage IV (route R3), in which weight loss is 10%. This stage was begun at about 150 and ended 220°C. This stage is supposed to be the decomposition of ferulic acid become vanillin [1];

- The stage V (route R3') (happening at between 220 and 270°C). The weight decreases gradually (about 20%). This is due to the decomposition of ferulic acid into vanillic acid [1].
- The stage VI (route R4). This stage occurs between 270 and 340°C. The weight loss was about 10%. This stage is the transformation of vanillin into vanillic acid [1].
- The stage VII. This is the last stage and starts from 340°C. After 450°C, the weight was relatively stable. Then, the mass degradation reached near to 30%. In this stage, there is the decomposition of all organic components into other smaller compounds (for example carbon) [1].

In addition, although the thermal decomposition reaction of turmeric can be predicted (see solid arrow routes in the panelled image), the existences of other reactions are possible (presented in dashed arrow routes in Fig. 3). Based on the thermal analysis, turmeric compound is relatively stable (both chemically and thermally) in the range of temperature of less than 100°C.

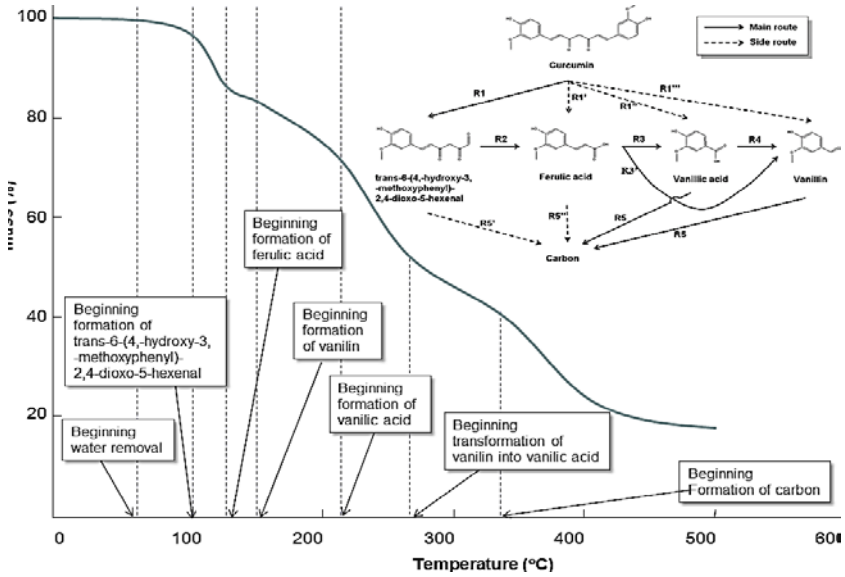

Fig. 3. Thermal analysis of the turmeric. The image panelled in the top-right figure is the possible route during the thermal decomposition process [1].

To confirm the above analysis, Fig. 3 presents the FTIR analysis of turmeric microparticles as a function of temperature. When heating at 100°C, the most changing peak is 3200 cm^{-1}. This peak is due to the water removal. The change of peak in the wave number of about 1500 cm^{-1} was found, confirming the beginning of the chemical decomposition process. The increases in heating temperatures of between 120 and 250°C resulted almost similar peaks and patterns. Some peak intensities increase, verifying the removal of some components. When heating sample at temperatures of more than 330°C, most of the peaks at 1500-2000 cm^{-1} disappeared, confirming the conversion of organic compounds into carbon. This result is also in a good correlation with the physical appearance of the sample, in

which the sample heated at more than 330°C is a black powder. This also gave ideas that there is no requirement for the further analysis for turmeric heated at more than 330°C.

Table 2 presents the comparison results between the experimental results and standard FTIR peaks in literature [15]. In Fig. 4, the FTIR analysis confirmed that all specimens (except sample heated at 330°C) had specific spectra. In short, the spectra were found in the wavenumber of about 1400 (corresponding to olefinic C–H bending vibration), 1500 (corresponding to C=C vibrations), as well as 1600 cm-1 (corresponding to C-O stretch). These spectra can be classified as turmeric component spectra [1].

Table 2. Comparison between FTIR spectra and literature [1].

Functional Group	Wavenumber (cm^{-1})	
	Experiment	**Reference**
Phenolic O–H stretching	3350	3510
C=C vibrations	1515	1627
C-O stretch	1635	1656
Olefinic C–H bending vibration	1400	1427
Aromatic C–O stretching vibrations	1165	1285
Aromatic C–O stretching vibrations	1165	1285
C–O–C stretching vibrations	1019	840 1027
C-H methyl ring	2976	2845
Aromatic ring	2932	3016

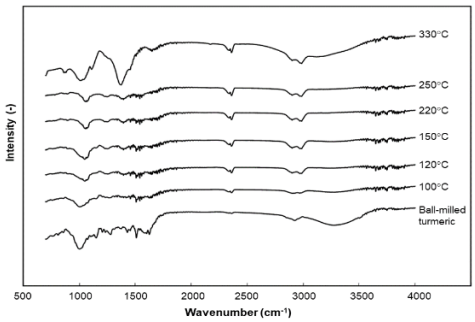

Fig. 4. The FTIR analysis of the turmeric microparticles heated at various temperatures.

4. Conclusion

In this study, we have successfully evaluated the thermal decomposition of turmeric microparticles under atmospheric condition. The result showed that turmeric is stable at temperature of less than 100^{o} C. The increases in the temperature affect to the decomposition of turmeric into its smaller molecular compound, such as curcumin, trans-6-(4, -hydroxy-3, -methoxyphenyl)-2,4-dioxo-5-hexenal; ferulic acid; vanillin and vanillic acid, and carbon. In addition, this study focused only on the impact of temperature on the physicochemical properties of micrometer-sized turmeric particles, and further parameters such as size will be done in the future work. However, the benefit obtained in this result will give better understanding

for the use of heat treatment in the turmeric and curcumin-related materials for food, drugs, and medical related uses.

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