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The effect of refining time to the antioxidant capacity, phenolic content, sensory and physical properties of dark chocolate couverture

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Abstract. Dark chocolate is one of the chocolate products which has the highest cocoa mass content around 60-70%. Dark chocolate has health benefits because of the high antioxidant content of phenol and flavonoids. The principle of making a chocolate bar is mixing and refining cocoa butter, liquor, and sugar. This research aimed to determine the effect of refining time on the characteristics of dark chocolate couverture. Cleared tests were carried out, consisting of the descriptive sensory test, preference test, texture using "Llyod" Testing Machine, color test using chromameter, and test of antioxidant activity and phenolic content. The test results state that the refining time process affects the organoleptic properties, color, and flavors. Refining time also affects for some parameters in texture, antioxidant capacity, and phenolic content antioxidant. Dark chocolate couverture that most preferred by the panelists is chocolate with 18 hours refining time, with antioxidant activity 68,96 ± 1,482 % and phenolic content 165,280 ± 1,558 mg GAE/mg.

Keywords: Dark chocolate, antioxidant capacity, phenolic content, sensory, physical properties.

1. Introduction

Cacao (*Theobroma cacao*) is a strategic role in the national economy which is the third largest contributor of foreign exchange for the plantation sector. In 2012, cocoa contributed to the foreign exchange reserves of US$ 1,053 billion, and the value increased from 2013 until now. Currently, Indonesia is the third sequence as world Cacao beans producer after Ivory Coast and Ghana. Indonesia has a target to become the largest producer in the next decade because there is still a wide land in Eastern Indonesia and reliable human resources. According to data from the Ministry of Agriculture 2017, the cacao productivity increased from the year 2016 of 785 kg/Ha, while 2017 of 787 kg/Ha. The cocoa production of 656.817 tons in 2016 increased to 688.345 tons in 2017. Therefore we need diversification to increased the added value of cocoa beans.

Chocolate is a product which is formulated from cocoa mass, cocoa butter, and sugar. Everyone consumed chocolate because it can generate sensory and positive emotions. Chocolate is categorized into 3 types, namely dark chocolate, milk chocolate, and white chocolate. Dark chocolate is one of the products of the chocolate couverture with a cacao content of more than 60%. Dark chocolate has benefits for health because the chocolate is rich in antioxidants namely phenol and flavonoid which are capable of capturing free radicals in the body. Antioxidant content on chocolate three times more than green tea.

These antioxidants are able to reduce the blood cholesterol so it can prevent the risk of heart attacks, cancer, high blood pressure, and stroke. Besides the cocoa butter is known as cholesterol free and does not obstruct the blood vessels [1].

There are five steps of dark chocolate processing, i.e., mixing, refining, tempering, molding, and packaging. The refining process is one of the critical points to obtain the fine and smooth chocolate. This research aims to find out the influence of the refining time on the quality of the dark chocolate couverture, namely sensory characteristic, texture, color, antioxidant activity, and phenolic content.

2. Material and Methods

2.1. Materials
The material used in this research is cocoa liquor, cocoa butter, and sugar. Cocoa liquor and cocoa butter obtained from farmers in the village of Nglanggeran, Gunungkidul, Yogyakarta. While sugar was obtained from the supermarket with the brand of Gulaku.

2.2. Dark Chocolate Processing
The making of dark chocolate covers 5 stages, i.e., mixing, refining, tempering, molding, and packaging. There were 3 different refining time formula, i.e., 16 hours, 18 hours and 20 hours. The analysis for each formula were organoleptic tests, antioxidant activity, total phenol test, texture, and color.

2.3. Sensory Evaluation
Hedonic tests were used to evaluate the sensory parameters. There were 30 panelists. The hedonic test was used to know the level of panelist preference with 7 scales. These scale from 7 to 1 were very like, like, quite like, just normal, quite not like, does not like, very does not like [2].

2.4. Texture and Color Measurement
The measurement of the dark chocolate texture by using the appliance Llyod texture analyzer which aims to know the value of violence chocolate on each treatment. While the color tests using Chromameter Konica Minolta CR 400.

2.5. Phenolic Content
Further samples according to Ruzaidi *et al.* [3] and Othman *et al.* [4] about 5-gram samples diluted with 25 ml alcohol 70%. Extraction is done at a temperature of 50 °C for 2 hours and then filtered to taken the filtrate. This Filtrate stored in a dark container at a temperature of 20 °C. Samples solution 0.2 ml mixed with 0.4 ml Folin-Cioalteuau for 5 minutes. Added 4 ml Na_2CO_3 7 % and aquadest until 10 ml total volume.The solution incubated at 23 °C for 90 minutes then the absorbance measured at λ 750 nm. Galic acid was used as a standard

2.6. Antioxidant Capacity
Analysis of antioxidant activity according to Ortega *et al.* [5] by mixing 250 µl sample solution with 5 ml 2.2-diphenyl 1-picrylhydrazyl (DPPH). The solution was homogenized and incubated for 20 minutes in the dark room. The absorbance was measured in λ 515 nm. Butylated hydroxytoluene (BHT) was used as a standard.

3. Result and Discussion

3.1. Sensory Evaluation
Three formula of dark chocolate couverture were tested organoleptically by 30 panelists. Based data on Table 1 in accordance with the parameters of color, flavors, taste, violence, tenderness and *overall*, then samples are the most preferred panelists is dark chocolate couverture with long mixing 18 hours compared with long mixing 16 and 20 hours.

Based on the parameters of colors and flavors, 16 hours refining time has a real difference with 18 and 20 hours, but 18 and 20 hours refining time is not different from each other. Panelist likes the color and aroma of dark chocolate couverture with 18 hours and 20 hours refining time (sig<0.05). This is due to the longer refining process, the color of dark chocolate more shiny and darker. The longer refining

or conching process will produce the finer dough, the color will even be distributed on the chocolate dough, and the surface area becomes larger. This allows the volatile escaping components that will provide a strong chocolate aroma impression. Aroma is one of the organoleptic characteristics which determines the level of consumer acceptance on a product. The delicious aroma can attract customers because it is a representation of a delicious taste [6].

Table 1 Panelists Preference against the Dark Chocolate Couverture

Refining time of dark chocolate	The Parameters					
	Colors	Aroma	Taste	Hardness	Smoothness	Overall
16 hours	4.20[a]	4.89[a]	4.51[a]	4.86[a]	4.24[a]	4.51[a]
18 hours	5.54[b]	5.58[b]	4.51[a]	4.35[a]	4.60[ab]	4.77[a]
20 hours	5.30[b]	5.56[b]	4.50[a]	4.86[a]	5.03[b]	4.56[a]

Description: letter a and b on each number showed that the sample is located on a different subset (p=0.05).

The parameter of taste, hardness and overall, there were no real difference in refining treatment time 16, 18 and 20 hours. Taste is the most important thing in the organoleptic characteristic of a product. The bitter taste is the natural taste of the chocolate. The bitter taste is derived from the alkaloid components such as *theobromine*.

The parameter of hardness and smoothness, there was no real difference in refining treatment time 16, 18 and 20 hours (<0.05). Refining time does not affect hardness and smoothness of chocolate. The hardness of 18 hours refining time has the lowest score; this indicates that this chocolate was not so hard. While the highest smoothness score found in dark chocolate which processed in 20 hours refining time. Good chocolate must have a smooth texture that can melt softly and gently in the mouth. Mixing and stirring in a long time can reduce the size of the chocolate particles. This affects the texture of chocolate. The large size of sugar particles is one of the causes of sandy and not a smooth texture. Therefore, we need refining or conching treatment process in a long time to reduce the size of the particles to the produced smooth texture of chocolate.

3.2. Physical Characteristics

The texture is part of the organoleptic characteristic of the product. The material which is not smooth and does not evenly mix will cause the rude texture of chocolate. This is the cause of the chocolate did not melt perfected in the mouth [7]. Tempering method will change the microstructures in the particle size of chocolate products. Particle size is inverse with texture and color, the bigger the size of particles, the more hardness of chocolate [8].

Table 2. The texture of dark chocolate Couverture

Refining time of chocolate	hardness bite 1 (N)	hardness bite 2 (N)	Cohesiveness (N)	Adhesiveness (Nmm)	Gumminess (N)	Fracture (N)	Springiness	Crispyness	Crunchiness (Nmm)
16 hours	338.68[a]	237.72[a]	0.4945[a]	61.91[a]	163.60[a]	129.75[a]	0.0060[a]	1.585.7[a]	413.415[a]
18 hours	583.76[a]	390.53[a]	0.3610[a]	79.24[a]	214.02[a]	416.85[b]	10.6050[a]	2.591.9[b]	1.088.65[a]
20 hours	606.25[a]	440.42[a]	0.4250[a]	61.91[a]	260.83[a]	496.54[b]	8.3350[a]	2.602.3[b]	963.245[a]

Description: letter a and b on the number shows that the sample is located on a different subset (p=0.05).

Hardness is the peak maximum at the first pressure on the bite. Based on the data Table 2, 16, 18 and 20 hours refining time does not provide the real influence on the value of the hardness bite 1 and hardness bite 2 (sig>0.05). Cohesiveness is defined as the ratio of the pressure area during the second compression until the first compression. Cohesiveness can be measured as the level where the materials were destroyed by mechanical. secondary parameters from the cohesiveness, among others brittleness, chewiness, and gumminess. Based on the data 16, 18 and 20 hours refining time does not provide the real influence on the value of the cohesiveness and adhesiveness (sig>0.05).

Gumminess is defined as the result of the hardness value multiplied by the value of the cohesiveness. Gumminess does not have the units. Based on the data 16, 18 and 20 hours refining time does not provide the real influence on the value of the gumminess (sig>0.05). Crispiness intensity is

defined as a sound when the first bite with the front teeth. Based on the data on the crispiness parameters and fracture, 16 hour refining time was different with 18 and 20 hours refining time, but 18 and 20 hours refining time were not different from each other. Springiness or elasticity can be interpreted as a recovery time between the end of the first bite and the beginning of the second bite. There are no units used because on this parameter calculating the difference in the area of time. Based on the data 16, 18 and 20 hours refining time does not provide the real influence on the value of the springiness (sig>0.05). Crunchiness is defined as the relation between fracture that has occurred on the next layer in the structure of the cells that give the impression of the expansion of the duration of the voice in time, 16, 18 and 20 hours refining time do not provide the real influence on the value of the crunchiness.

Table 3 The color of dark chocolate Couverture

Refining time of samples	The average value			ΔE
	L	A	b	
16 hours	29.31^c	8.83^c	5.55^c	31.11^c
18 hours	27.94^a	7.03^b	3.69^b	29.05^a
20 hours	28.63^b	6.67^a	3.21^a	29.57^b

Description: Letter a, b and c on the numbers shows that the sample is located on a different subset (p=0.05).

The code: ΔL = difference between light and dark, A = Δ differences in red and green, Δb = difference between yellow and blue, ΔE = total difference colors

Consumers prefer chocolate with a dark color, shiny, not fade and not blooming in its surface [9]. Table 3 showed the results of the color test using chromameter that produces the value of the L, a and b. The ΔE value of samples 16, 18 and 20 hours refining time were 31,10; 29,05 and 29.57. The value of ΔE on each sample different from each other. The results of the test statistic obtained that there was a real difference to the value of ΔE on each treatment (sig<0.05).

In Table 4. known that total phenolic content of dark chocolate couverture with refining time 16, 18 and 20 hours in a row of 105.924 ± 4.337 mg GAE/gram samples, 165.280 ± 1.558 mg GAE/gram samples and 154.900 ± 5.022 mg GAE/gram samples. While Natsume *et al*. [10] reported that the average of total phenol dark chocolate in all countries was 578.64 mg CAE/100 g (CAE = Catechin Equivalent). The biggest total phenolic content on 18 hours refining time chocolate, while the smallest total phenolic content on 16 hours refining time chocolate. The statistics result obtained that there was a difference between the total phenol on each chocolate formula (Sig.≤0.05). The total phenolic content of the beans and cocoa products is very influenced by the interaction of genetic factors with their surroundings. In the period before the harvest (pre-harvest) total phenolic content influenced by the interaction of genetic factors (genotype/varieties/clone) with environmental factors biophysics or agronomist (aquaculture). Later in the period of post-harvest, the components of the post-harvest interact each other with processing factors (the process of fruit storage, fermentation, drying, and roasting) to influence polyphenol content [11].

Table 4 Total Phenolic Content of Dark chocolate Couverture

Refining time	The total content of GAE phenol (mg/gr samples)
16 hours	105.924 ± 4.337^a
18 hours	165.280 ± 1.558^c
20 hours	154.900 ± 5.022^b

Description: letters a, b and c on the numbers shows that the sample is located on a different subset (p=0.05)

According to Harrington [12] the polyphenol content in chocolate products will provide benefits for the improvement of the quality of the product. This due to the polyphenol compounds has antioxidant capabilities that can prevent food oxidation of cacao butter that can cause rancidity. This will increase the shelf life of chocolate products.

Table 5 Antioxidant Activity Dark chocolate Couverture

Refining time	%Inhibition of radical DPPH
16 hours	$55.01 \pm 0.703a$
18 hours	$68.96 \pm 1.482b$
20 hours	$60.87 \pm 1.482c$
BHT solution	$53.77 \pm 0.458a$

Description: letters a, b and c on the numbers shows that the sample is located on a different subset (p=0.05)

Analysis of the antioxidant activity of three formula *dark chocolate* using radical scavenging DPPH methods. Data on Table 5 showed that the antioxidant activity of dark chocolate couverture with 16, 18, 20 hours refining time in a row of 55.01 ± 0.703 %; 68.96 ± 1.482 %; and 60.87 ± 1.482 %. While BHT solution as standard showed the antioxidant activity of 53.77 ± 0.458 %. The biggest antioxidant activity on 18 hours refining time dark chocolate. While the smallest antioxidant activity was 16 hours refining time dark chocolate. The statistics result obtained that there were very real differences in the antioxidant activity of each formula (Sig.$\leq$0.05). According to Genovese [13], antioxidant activity on the dark chocolate in Brazil by 7.8 ± 0.4 %. Antioxidant activity and total phenol in this study different from previous research because of the difference of cocoa bean. The different varieties, environment plant, and cacao processing will affect the level of antioxidants and phenol on chocolate products.

There is a positive correlation between the antioxidant capacity of cacao and its products with the number of total polyphenols. The lower of polyphenol content, the lower the value antioxidant capacity [14]. The heating process high tends to decrease the polyphenol content in the samples. Some polyphenol compounds found in cacao beans are :

(1) hydroxybenzoic acid(gallic god syringic, protocatechuic, vanillic acid),
(2) hydroxycinnamic acid (caffeic, ferulic, p-coumaric, phloretic acids, clovamide, dideoxyclovamide),
(3) flavonols (quercetin),
(4) flavones (luteolin. apigenin),
(5) flavanones (naringenin), and
(6) flavanols (catechin, epicatechin, procyanidins/oligomers, and polymers)

4. Conclusion

Based on this research data, dark chocolate couverture with 18 hours refining time become the most preferred formula. Its characteristic was the activity of antioxidant 68.96 ± 1.482%, total phenolic content 165.280 ± 1.558 mg GAE/mg, hardness bite 1 583.76 N, hardness bite 2 390.53 N, cohesiveness 0.3610 N, adhesiveness 79.24 Nmm, gumminess 214.02 N, fracture 416.85 N and the value of the L, a and b respectively 27.94; 7.03; and 3.69.

5. Acknowledgment

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