

## The utilization of cocoa polyphenol extract to improve the shelf life of bulk frying oil used in open and deep frying

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### Abstract

Bulk Frying Oil (BFO) derived from semi-purified crude palm oil is widely used in Indonesia. Different from refined-bleached-deodorized palm olein that usually undergo full purification and fractionation, BFO is considered as lower quality because it still contains soft stearin fraction. Long shelf life and the reusability of frying oil could be improved by the addition of synthetic antioxidant such as BHA (butylated-hydroxyanisole), BHT (butylated-hydroxytoluene) and TBHQ (tertiary-butyl-hydroquinone). However, synthetic antioxidants utilization is being replaced with natural compound due to the rising health concerns. Polyphenol is a natural antioxidant which is commonly found in cocoa bean and had reported to exhibit an ability to retard lipid oxidation. This research was aimed to study the effect of polyphenol extracted from unfermented cocoa bean to extend shelf life and reusability of bulk frying oil. Central Composite Design of Response Surface Methodology was used to study the effects of polyphenol concentration and frying frequency in open and deep frying of soybean tofu. Results showed that the addition of polyphenol extract was able to retard the formation of free fatty acids and peroxide value during frying process and maintain the clarity of the oil. The optimization study revealed that the addition of 0.04% polyphenol extract could prolong the usage of oil up to 8 times when utilized in open frying. On the other hand, only 0.01% of polyphenol extract is needed to prolong the oil usage up to 20 times when it was applied in deep frying method.

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### Keywords

Polyphenol

Cocoa bean

Oxidation

Scavenging activity

Response surface

methodology

Deep frying

Open frying

### Introduction

Bulk Frying Oil (BFO) derived from crude palm oil (CPO) plays an important role in cooking process and it is considered as one of the most popular frying oil in Indonesia (Wiyati, 1992). According to Ketaren (1986) and Fellows (2000), the function of frying oil is not only as media for heating, but also increases the palatability and improves the nutritional value of food product. Two types of frying oil that are commonly used in Indonesia, i.e. refined frying oil (RFO) and bulk frying oil (BFO). RFO is obtained from the fractionation of refined-bleached-deodorized palm oil, which results in liquid olein fraction and solid stearin fraction. This oil is usually sold in branded packaging. BFO is an un-fractionated refined-bleached-deodorized palm oil, considered as a lower quality. It still contains soft stearin fraction that affect its clarity (Che Man *et al.*, 1999). Currently, BFO is preferred by consumers because it is cheaper compared with RFO palm olein.

Palm-based oil is known as heavy-duty frying oils due to its good oxidative stability resulted from its high proportion of unsaturated and monounsaturated fatty acids (Nallusamy, 2006; Fan *et al.*, 2013). However, high heat treatment during frying process could affect

degradation process such as hydrolysis, oxidation and polymerization (Ketaren, 1986; Fellows, 2000). Repeated use of cooking oil has become a common practice in order to reduce frying cost. However, the repeated uses could lead into the development of lipid oxidation, hydrolysis and polymerization product that resulted in rancidity and oil breakdown. These lipid degradation products were also reported to give an adverse effect on human health such as gastrointestinal problem and cancer (Ketaren, 1986; Shahidi and Wanasundara, 1992; Maillard *et al.*, 1996).

Synthetic antioxidant such as BHA (butylated-hydroxyanisole), BHT (butylated-hydroxytoluene) and TBHQ (tertiary-butyl-hydroquinone) are usually added into the oil to retard the degradation process (McWilliams, 2001; Shahidi and Zhong, 2005). Despite the fact that synthetic antioxidant is proven to be effective, its usage is becoming more obsolete. The use of synthetic antioxidants in food products is under strict regulation due to the potential health hazards caused by such compounds (Hettiarachchy *et al.*, 1996). Several researchers have found that the molecules of synthetic antioxidant are hazardous to human health (Williams, 1993; Moktan *et al.*, 2008).

Polyphenol is a complex of phenolic compound

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that able to act as antioxidant through its reaction with free radicals and chelate the metal ions which could trigger the oxidation process (Bravo, 1998). Unfermented cocoa beans are reported to contain high concentration of polyphenol, in which its concentration was then reduced during cocoa bean fermentation and drying (Misnawi, 2003). Flavan-3-ol, anthocyanin and procyanidine were identified as major polyphenol compound in cocoa where catechins and epicatechins are the main component of procyanidine (Weisburger, 2005). In the lipid body, these phenolic compounds are able to retard the lipid oxidation by donating a hydrogen atom or an electron to chain initiating free radicals such as the hydroxyl and superoxide radicals (Cao *et al.*, 1997; Prior and Cao, 2000; Shahidi and Wanasundara, 2008). They also neutralize the substrate-derived free radicals such as the fatty acid free radicals and alkoxy radicals (Cao *et al.*, 1997). Incorporation of such extract in human foods not only preserves their wholesomeness, but also reduces the risk of developing atherosclerosis and cancer (Ames, 1983; Namiki, 1990; Ramarathnarn *et al.*, 1995).

The application of natural antioxidant in cooking oil has been previously reported (Suja *et al.*, 2004; Merrill *et al.*, 2008). However, the application of polyphenol extracted from unfermented cocoa bean has not been published. Previous research has mentioned that polyphenol from cocoa beans relatively resistant to heat (Misnawi *et al.*, 2002). Thus, it is suitable to be applied as additive for BFO. This research aimed to study the effect of cocoa polyphenol in retardation of the oxidation in bulk frying oil.

## Material and Methods

### *Polyphenol extract*

Polyphenol extract was prepared according to the method of Misnawi (2003). Unfermented cocoa beans were dried to reach moisture content of 7.5%. The beans were then deshelled and the cotyledons obtained were powdered, before defatted with petroleum benzene solvent in soxhlet apparatus. Defatted cocoa powder was then mixed with ethanol-distilled water mixture (1:3) and incubated for 24 hours at room temperature. The mixture was then filtered using filter paper. The polyphenol extract 310 mL was obtained by evaporating the 6700 mL of supernatant by using rotary evaporator. 30 mL of the liquid polyphenol extract was then stored to vacuum dessicator resulted in 15.43 g of polyphenol extract powder.

### *Total phenolic content*

Total phenolic in polyphenol extract was determined according the method of Szydłowska-Czerniak (2008) with slight modifications. Finely weighted polyphenol extract (0.2 g) was transferred into test tube and added with 1 mL ethanol, 4.8 mL distilled water and 0.5 mL Follin-Ciocalteau (50%) reagent. The mixture was then vortexed and rested for 5 minutes. To the extract, 1 mL of saturated sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) was added and the solution was made up to 10 mL with distilled water. After rested for 1 hour in dark room, the absorbances of the solutions were measured using a UV-160A spectrophotometer (Shimadzu Corp., Nagakyo-Ku, Kyoto, Japan), measured at 725 nm against a reagent blank. (-)-Epicatechin (0 - 200 mg/L) was used as standard in calibration curve preparation.

### *Experiment condition*

The experiment was conducted according the design suggested by Design-Expert software version 7.0 (Stat Ease, Minneapolis, MN, USA) using face centered central composite design (CCD). The independent variable were the frequency of frying ranged from 0 (no frying) to 20 times of frying and polyphenol concentration added into the BFO ranged from 0% (no addition) to 0.04%. Frying treatment was carried out using 2 L of polyphenol fortified-BFO to fry 10 local tofus in fryers with total capacity of 4 L. The frying method was divided into open frying (OF) and deep frying (DF).

### *Free fatty acid*

FFA was determined using the method of AOCS Ca 5a-40 (AOCS, 1998). Approximately, 2 mL oil was transferred into a flask followed with neutralized 95% ethanol and 2 mL of phenolphthalein indicator (1%). The solution was then mixed using magnetic stirrer. The mixture was then titrated with sodium hydroxide solution 0.1 M until a permanent pink color persisted for at least 30 s. Concentration of FFA was calculated as oleic acid basis.

### *Peroxide value*

The peroxide value (PV) was determined using the official method of AOAC 965.33 (AOAC, 2000). Thirty milliliters of chloroform/acetic acid 3:2 (v/v) was used to dissolve a known weight of oil sample (2 g). Approximately 0.5 mL freshly prepared saturated KI solution was then added to the mixture and then vortexed for exactly 1 min. Distilled water (30 mL) and starch indicator (0.5 mL, 1%) were added and

Table 1. Face centered experimental design in coded (a and b) and actual level (A and B) of variables

Expt. No	Frequency (times)		Concentration(%)		Open Frying			Deep Frying				
	Coded Level a	Actual Level A	Coded Level b	Actual Level B	FFA	PV	Clarity	DPPH	FFA	PV	Clarity	DPPH
1	0	10	0	0.02	0.0999	12.000	70.400	16.370	0.1044	5.000	61.300	36.190
2	1	20	0	0.02	0.1339	16.233	55.050	8.420	0.1146	5.991	52.275	7.360
3	0	10	0	0.02	0.0999	12.000	69.800	16.500	0.0998	4.000	63.100	18.390
4	0	10	-1	0.00	0.1407	18.722	60.600	0.000	0.1339	7.250	56.500	0.000
5	-1	0	-1	0.00	0.1248	1.997	96.200	0.000	0.1021	2.249	98.975	0.000
6	0	10	1	0.04	0.0953	10.740	70.900	25.190	0.0953	3.244	65.850	44.260
7	1	20	1	0.04	0.1112	13.237	55.750	17.270	0.1066	4.239	46.700	28.030
8	0	10	0	0.02	0.0999	12.974	70.200	16.250	0.1089	5.988	60.000	29.910
9	0	10	0	0.02	0.1089	13.972	69.700	15.720	0.1089	4.000	61.000	26.040
10	-1	0	1	0.04	0.0851	1.997	85.900	39.430	0.0907	1.995	94.825	60.060
11	1	20	-1	0.00	0.1690	21.489	51.375	0.000	0.1492	9.245	42.600	0.000
12	0	10	0	0.02	0.1021	12.737	70.025	16.210	0.1055	4.747	61.350	27.630
13	-1	0	0	0.02	0.0976	2.000	90.575	23.780	0.0919	1.996	96.950	38.820

FFA: mg KOH/g fat  
 PV: MeqO<sub>2</sub>/kg fat  
 Clarity: Percentage of transmittance  
 DPPH: %

then titrated with sodium thiosulfate (0.1 M) until the blue color was disappeared.

#### Oil clarity

Oil clarity was analyzed employing a UV-160A spectrophotometer (Shimadzu Corp., Nagakyo-Ku, Kyoto, Japan), measured at 583 nm. The clarity was determined according the percentage of transmittance detected by the spectrophotometer.

#### DPPH radical scavenging activity

Radical scavenging activity (RSA) analysis was performed based on the activity of the 2,2-diphenyl-1-picrylhydrazyl (DPPH). This analysis was carried out using the method of Gadov (1996) with some modification. Approximately 0.2 g of sample was dissolve in 20 mL of ethanol and stirred for 10 minutes. The solution was then centrifuged for 3 min at 5,000 rpm. Approximately 1 mL of the filtrate placed into a test tube and mixed with 0.5 mL DPPH reagent and then shaken vigorously. The solution was then placed in a dark condition for 20 min. After that, the solution was fixed up to 5 mL using ethanol. The absorbance of the sample mixture was then measured at 517 nm using a UV-160A spectrophotometer (Shimadzu Corp., Nagakyo-Ku, Kyoto, Japan). Antioxidant activity was presented as % scavenging activity according the following formula:

$$\%RSA = ((\text{Abs blank} - \text{Abs sample}) / \text{Abs sample}) \times 100\%$$

#### Statistical analysis and optimization

The experiment was carried out by two variables (three levels of each variable), face centered central composite design with five replications at the center points. The levels of variable were coded at (-1, 0, +1). The independent variables were frequency (A), and polyphenol concentration (B). The experiment design is shown in Table 1. Statistical analysis was carried out using Design Expert® version 7.0.0 (Stat-

Ease, Inc., Minneapolis, MN, USA). The model was performed at 5% significance level in which  $p < 0.05$  was considered as significant parameters and non-significant parameters ( $p > 0.05$ ) were excluded. The response function Y for all responses was fitted to a second-degree polynomial using below equation:

$$Y = b_0 + b_1A + b_2B + b_{12}AB + b_{11}A^2 + b_{22}B^2 + \varepsilon$$

The linear, quadratic, and interaction effects was represented along with the coefficient ( $b_0$ ) by  $b_1$ ,  $b_2$ , (linear effects),  $b_{12}$  (interaction effects), thus  $b_{11}$ , and  $b_{22}$  for quadratic effects. The optimum condition for the chosen desired goal is decided using Myers and Montgomery desirability method contained in the software in purpose to obtain minimum FFA and PV and maximize the Clarity and DPPH RSA.

#### Result and Discussion

Preliminary analysis on total phenolic content (TPC) of polyphenol extract from cocoa bean in comparison with (-)-epicatechin standard resulted in the TPC of polyphenol extract found 172.75 g eq (-)-epicatechin/kg bean. This result was in agreement with previous research carried out by Misnawi (2003) which found that polyphenol concentration in defatted unfermented cocoa bean was in range of 120 – 180 g eq (-)-epicatechin/kg.

The results of dependent variable those were carried out according the design of CCD are presented in Table 1, in which the RSM analysis was done separately between the responses in open frying and deep frying. Table 2 shows the summarized analysis of variance (ANOVA) regarding the model fitting (model, lack of fit,  $R^2$  and adjusted  $R^2$ ), the model equation and significant factors for each responses. All of the responses showed that the quadratic model is significant, mean that the additions of quadratic terms were significantly improved the model

Table 2. Summarized ANOVA of the variables according central composite design (CCD)

Parameters	FFA		PV		Clarity		DPPH RSA	
	OF	DF	OF	DF	OF	DF	OF	DF
Model	Quadratic significant	Quadratic significant	Quadratic significant	Quadratic significant	Quadratic significant	Quadratic significant	Quadratic significant	Quadratic significant
Lack of fit	not significant	not significant	not significant	not significant	not significant	not significant	Significant	not significant
R <sup>2</sup>	0.981	0.961	0.979	0.936	0.969	0.985	0.992	0.938
Adjusted R <sup>2</sup>	0.968	0.933	0.965	0.890	0.946	0.974	0.987	0.894
Equation (Actual levels)	$Y=0.126+0.0004A-0.00009A^2+28.68B^2$	$Y=0.11+0.0027A-1.28B-0.04AB$	$Y=3.075+1.82A-162.5B-10.32AB+3249.1B^2$	$Y=2.59+0.5A-64.85B-5.94AB$	$Y=93.01-3.123A+0.05A^2$	$Y=96.78-4.99A+0.115A^2$	$Y=0.95-0.213A+1239.3B-27.7AB-6997.8B^2$	$Y=1.77+0.223A+1839.4B-0.038AB$
Significant factor	A, B, A <sup>2</sup> , B <sup>2</sup>	A, B, AB, B <sup>2</sup>	A, B, AB, A <sup>2</sup>	A, B, AB	A, A <sup>2</sup>	A, A <sup>2</sup>	A, B, AB, B <sup>2</sup>	A, B, AB

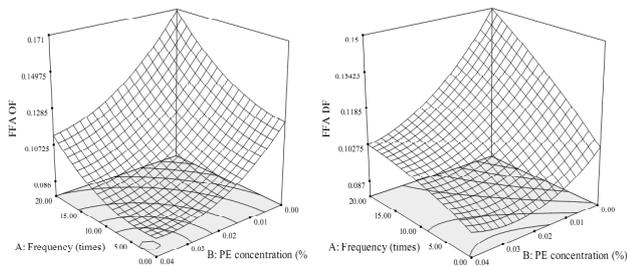


Figure 1. *Left*: Response surface for the effect of PE concentration and frying frequency on the FFA of open frying oil. *Right*: Response surface for the effect of PE concentration and frying frequency on the FFA of deep frying oil.

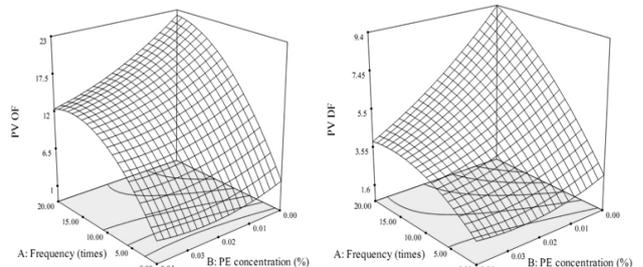


Figure 2. *Left*: Response surface for the effect of PE concentration and frying frequency on the PV of open frying oil. *Right*: Response surface for the effect of PE concentration and frying frequency on the PV of deep frying oil.

adequacy (Herpandi *et al.*, 2013). Even though the model were significant, several responses resulted in significant value of lack of fit (Clarity OF and DF, and DPPH RSA OF) which represent that the quadratic model was not suitable for the respective responses. The entire quadratic models suggested resulted in high R<sup>2</sup> and adjusted R<sup>2</sup> (adj-R<sup>2</sup>) that were more than 0.89. Little & Hills (1978) and Koochecki *et al.* (2009) previously mentioned that the R<sup>2</sup> should not be less than 0.80 and must be followed by close value of adj-R<sup>2</sup> to make sure that non-significant terms was excluded and the model is adequate. Since the model of Clarity OF & DF, and DPPH RSA OF could not become good indicators, these models were not used in optimization.

#### Effect of cocoa polyphenol in open frying

On the lipid body, free fatty acids occurred mainly due to the hydrolysis process in the presence of water. This hydrolysis process breakdown the triglycerides into glycerol and free fatty acids (Ketaren, 1986; Wiyati, 1992; Melton *et al.*, 1994). Fellows (2000) previously stated that the oil decomposition could lead to the potential toxic material and nutritional changes. Indonesian National Standard (SNI 1-3741-1995) (BSN, 1995) allows the FFA content of commercial frying oil up to 0.3%. This standard is similar with those of CODEX (CODEX STAN 210-1999) which limits the FFA content up to 0.3% and peroxide value up to 10 meqO<sub>2</sub>/kg oil. Result of FFA analyses in this experiment resulted in lower concentration of FFA compared to aforementioned. The FFA concentrations

in open frying oil were in range of 0.0851 to 0.1690%. As shown in Figure 1, the addition of polyphenol extract to BFO could retard the formation of FFA in bulk frying oil used in open frying. The addition of 0.04% polyphenol extract resulted in significantly lower concentration of FFA (0.1135%) even though the oil had been used for 20 times. In comparison with BFO without addition of polyphenol extract, the FFA reached 0.169% after being used for 20 times. Melton *et al.* (1994) and White (1991) previously mentioned that during frying process the FFA concentration is increasing due to the oxidation and hydrolysis occurred in the lipid body. This result showed that the addition of polyphenol extract to the BFO could effectively retard the formation of FFA during frying process. The polyphenol could scavenge the free radicals, thus retard the formation of FFA by limiting the oil oxidation (Cao *et al.*, 1997; Shahidi and Wanasundara, 2008).

Peroxide values (PV) also showed similar trend to that of FFA. PV was found to range from 2 to 21.489 MeqO<sub>2</sub>/kg oil, that is much higher than that of CODEX limit (<10 MeqO<sub>2</sub>/kg oil). High degradation rate of oil in open frying condition could be affected by higher food:oil contact surface ratio, higher exposure to atmospheric oxygen and lower temperature control under processing (Andrikopoulos *et al.*, 2002b). Shahidi and Warasundara (2008) mentioned that the formation of lipid-peroxide complex could be initiated by singlet/triplet oxygen radicals or by free radicals generated from previous propagation steps of oxidation. Antioxidant is able to retard the oxidation

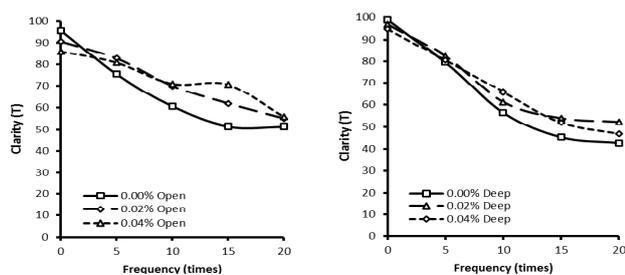


Figure 3. *Left*: Graph for the relation between PE concentration and frying frequency on the Clarity of open frying oil. *Right*: Graph for the relation between PE concentration and frying frequency on the Clarity of deep frying oil.

process by forming a stable phenoxy radical complex with propagation steps product. With the absence of radicals, the hydroperoxides were forced to process into the termination steps resulting in stable compound which minimize further propagation of oxidation (Bravo, 1998). As shown in Figure 2, the additions of polyphenol extract significantly reduced the oxidation rate of BFO during frying. The frying oil without the addition of polyphenol extract exhibited high increase in PV up to 21.489 MeqO<sub>2</sub>/kg oil as the frying frequency increased to 20 times. In contrast, the increase of the polyphenol concentration added to the oil, the more resistant the oil to the oxidation resulting in lower PV up to 12.65 MeqO<sub>2</sub>/kg oil.

Das and Pereira (1990) mentioned that the development of brown color in frying oil is normally associated with oxidation and polymerization. Figure 3 shows the clarity of BFO was decreased as the increase in frequency of frying, in which the steeper decrease rate was observed in the BFO without the addition of polyphenol. BFO added with polyphenol extract after 20 times of frying showed higher clarity compared to non-added BFO without polyphenol addition, i.e. at 55.75 and 51.375, respectively. This oil exhibited less intense in the decreasing rate. Hence, it proved that the addition of polyphenol could maintain the clarity of BFO due to its activity towards oxidation.

DPPH RSA analysis showed that the polyphenol addition into BFO suppressed the formation of radicals during frying. The decrease percentage of antioxidant activity were 64.59% after 20 times of frying i.e. 23.78 to 8.42% DPPH RSA at 0.02% PE, whereas the decrease percentage of antioxidant activity of BFO added with 0.04% PE were 56.2% after 20 times of frying i.e. from 39.43 to 17.27% DPPH RSA (Figure 4). This decrease proved that the polyphenol in BFO was actively used to retard the oil breakdown during frying process. As the increase in frying frequency, more of antioxidant was used; thus resulted in the decrease of the DPPH RSA due

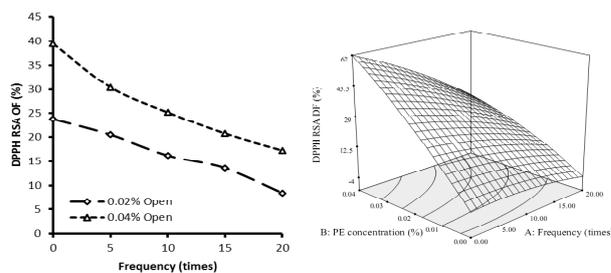


Figure 4. *Left*: Graph for the relation between PE concentration and frying frequency (times) on the DPPH RSA of open frying oil. *Right*: Response surface for the relation between PE concentration and frying frequency on the DPPH RSA of deep frying oil.

to the lower active antioxidant compound left in the oil. This result was in agreement with the report of Andrikopoulos *et al.* (2002a) who found that the deterioration of phenolic compound happened during successive frying of virgin olive oil. Quiles *et al.* (2002) also mentioned that as the frying time increased, the antioxidant potential of rich-phenolic-virgin olive oil was also decreased. However, BFO with the addition of 0.02 and 0.04% PE still exhibited relatively high RSA even though already processed up to 20 times frying i.e. at 8.42 and 17.07% RSA, respectively, representing their potential to retard the oil oxidation process in further frying process.

#### Effect of cocoa polyphenol in deep frying

The FFA concentration of BFO used in deep frying were slightly lower compared to those of open frying, ranged from 0.919 to 0.1492%. On the other hand, the PV of BFO used in deep frying shows different result with that of open frying. The PV of DF ranged from 1.996 to 9.245 MeqO<sub>2</sub>/kg oil, much lower than that of open frying (2-21.489 MeqO<sub>2</sub>/kg oil). Andrikopoulos *et al.* (2002a) previously found that deep-frying method resulted in better recoveries of oxidative deterioration product compared to open-frying. These differences are suspected to be contributed by the different cooking style and equipment during experiment. This experiment used large shallow pan type fryer which allowed wider contact area with air; whereas in deep frying treatment, it used deeper smaller pan. This was in agreement with Kalogeropoulos *et al.* (2007) who mentioned that the pan-frying caused higher oxidized fatty acid and polymerized triacylglycerol compared to deep frying due to higher surface area which contacted with air. Moreover, open frying required a stirring process which intensified the contact between oil and air resulted in higher oxidation rate compared to deep frying which only need minimum stirring (Santos *et al.*, 2013).

The addition of PE into the BFO effectively retard

the formation of free fatty acids and lipid-peroxide complex, resulting lower FFA and PV compared to that without the addition of polyphenol. As shown in Figure 1, the addition of polyphenol extract into BFO could retard the formation of FFA up to 0.114% (0.04% PE, 20 times frying) compared to those without the addition of polyphenol (0.1492%, 20 times frying). On the longest frying frequency (20 times), 0.04% polyphenol could limit the formation of lipid-peroxide complex as low as 3.916 MeqO<sub>2</sub>/kg oil. Without the addition of polyphenol, the PV of BFO could reach 9.245 MeqO<sub>2</sub>/kg oil (Figure 2). As the decrease in oxidation rate, the polyphenol added-BFO also possessed higher clarity (52.275 for 0.04% PE and 46.7 for 0.02% PE) compared to BFO without polyphenol (42.6) (Figure 3).

DPPH RSA of BFO added with cocoa polyphenol exhibited decrease trend as the increase of frying frequency (Figure 4). After 20 times successive frying, antioxidant activity of BFO added with 0.02% of polyphenol decreased 31.46 units (from 38.820 to 7.360% DPPH RSA). On the other hand, the loss as much as 32.03 unit (from 60.06 to 28.03% DPPH RSA) was exhibited by BFO added with 0.04% cocoa polyphenol, relatively higher compared to that of open-frying (15.36 and 22.16 units for 0.02% PE and 0.04% PE, respectively). These different losses were reflected on the oxidative retardation of BFO on respective treatment, in which deep frying treatment resulted in higher oxidative stability compared to open frying. These results also indicated that the oxidation rate in open frying was higher than polyphenol scavenging capacity, mainly caused by the wider contact area of BFO with air resulting in intense oxidation process. However, BFO added with 0.04% still showed high antioxidant activity after successive 20 times frying (20.83% DPPH RSA) which indicated the possibilities to be used for more frying.

#### Optimization study

Numerical optimization was done based on the purpose of minimizing the FFA and the PV for possible longest frying frequency while utilized minimum amount of polyphenol extract. The CODEX Standard (CODEX STAN 210-1999) was used as limiter for oil quality (FFA <0.3%, and PV <10 MeqO<sub>2</sub>/kg oil). Optimization on open frying treatment resulted in optimum condition of 0.04% of polyphenol extract which able to prolong the oil reusability up to eight times without exceeding the CODEX STAN 210-1999 quality limitation. Without the addition of polyphenol, the reusability of BFO in open frying treatment was limited for only five times

of frying.

On the other hand, the additions of 0.01% polyphenol extract was sufficient to prolong the oil usage in deep frying method up to 20 times without exceeding the limitation of the CODEX STAN 210-1999, or 0.04% was needed if measured against AOCS standard (PV <5 MeqO<sub>2</sub>/kg oil). In contrast, without the addition of polyphenol, the reusability of BFO in deep frying treatment was limited for only five times of frying (measured against AOCS standard, PV <5 MeqO<sub>2</sub>/kg oil).

CODEX STAN 210-1999 has limited the usage of antioxidant in frying oil on different proportion. The usage of synthetic antioxidant such as TBHQ, BHA, and BHT is limited up to 120, 175, and 75 mg/kg of frying oil, whereas the use of naturals such as ascorbyl palmitate is up to 500 mg/kg. However, the usage of other natural antioxidant such as tocopherol was not limited. It is relevant to the regulations known as Good Manufacturing Practices (GMP) which allows the manufactures to use the amount of additive necessary to achieve the desired results. In this study, the addition of polyphenol was ranged from 0.01% to 0.04% which were equivalent to 100 to 400 mg/kg. Thus, the usage of polyphenols is still acceptable since 0.01% of polyphenol (100 mg/kg) had already resulted the desired effect. The usage on this value in frying oil product is much lower compared to the limitation of antioxidant usage as aforementioned.

#### Conclusion

This study proved that the utilization of polyphenol extract obtained from unfermented cocoa bean could substitute the synthetic antioxidant compounds to preserve the BFO. The additions of polyphenol extract significantly improved the oxidative stability of BFO. The polyphenol extract of 0.04% could prolong the usage of oil up to eight times when utilized in open frying. On the other hand, only 0.01% of the polyphenol extract is needed to prolong the oil usage up to 20 times in deep frying. This information could be used by households and food industry to find an alternative of cheaper and more efficient frying oil preservation.

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