International Food Research Journal 24(3): 1270-1277 (June 2017)
Journal homepage: *http://www.ifrj.upm.edu.my*

Photo-oxidative changes of red palm oil as affected by light intensity

[1,2]Ayu, D. F., [1,3*]Andarwulan, N., [1,3]Hariyadi, P. and [1,3]Purnomo, E. H.

[1]*Department of Food Science and Technology, Bogor Agricultural University, 16680 Bogor, Indonesia*
[2]*Department of Agricultural Technology, Riau University, 28293 Pekanbaru, Indonesia*
[3]*Southeast Asian Food and Agricultural Science and Technology (SEAFAST) Center, 16680 Bogor, Indonesia*

Article history

Received: 4 January 2016
Received in revised form: 17 April 2016
Accepted: 17 May 2016

Keywords

Carotene
Chlorophyll
Photo-oxidation
Red palm oil
Total tocopherol

Abstract

The objective of this research was to study the effect of light intensity on photo-oxidative stability of red palm oil (RPO). Photo-oxidation was investigated under elevated intensity of fluorescent light of 5,000, 10,000 and 15,000 lux for 7 d at 31±2°C. Minor compounds (chlorophyll, total tocopherol, carotene) and oxidative stability parameters (peroxide, p-anisidine and total oxidation values) of oil were evaluated daily. Chlorophyll and total tocopherol decreased during 7 d of light exposure in which their degradation was proportional to the light intensity. However, photodegradation of carotene was not observed. Photo-oxidation of RPO was also indicated by the increase of peroxide and total oxidation values. Their increase rates were higher at higher light intensity which can be described using zero order kinetics model. On the other hand, p-anisidine value was not sensitive to indicate the photo-oxidation in RPO. Significant negative correlation between peroxide value and total tocopherol changes indicated that the peroxide value was more sensitive to the changes of total tocopherol at higher light intensity.

Introduction

Palm oil is currently one of the most consumable edible oil in the world, with Malaysia and Indonesia being the top two producers (Mba *et al*., 2015). Palm oil is characterized with its high content of carotenoids and vitamin E. Refining process without bleaching to produce red palm oil (RPO) has been developed. RPO has carotenoids content of 524 mg/kg and vitamin E (tocopherols and tocotrienols) as high as 955 mg/kg (Yi *et al*., 2011). Carotenoids of RPO are mainly composed of β-carotene which is a precursor of vitamin A (Yi et al., 2011). Rice and Burns (2010) pointed out that RPO was highly efficacious in improving vitamin A status among populations at risk of vitamin A deficiency. Vitamin E in palm oil consists of 21% α-tocopherol, 26% α-tocotrienol, 40% γ-tocotrienol and 13% δ-tocotrienol which act as potent biological antioxidants, protectors against oxidative stress and atherosclerotic process (Mukherjee and Mitra, 2009; Idris *et al*., 2014).

The other important group of pigment besides the carotenoids in palm oil is chlorophyll (Sambanthamurthi *et al*., 2000). Like the carotenoids, chlorophyll pigments are partially removed by bleaching earths in a conventional processing. However, refining process still maintains low level of chlorophyll content in commercial palm oil (Usuki *et al*., 1984). The presence of chlorophyll, tocopherols, tocotrienols and β-carotene has an important role in the stability of RPO. Chlorophyll acts as a photosensitizer (Lee *et al*., 1997; Choe and Min, 2006). After absorbing light energy, chlorophyll transfers the energy to triplet oxygen and turns it into reactive singlet oxygen (Min and Boff, 2002). Singlet oxygen will attack C=C bond to produce peroxides, initiating series of auto-oxidation reaction that produces more hydro-peroxides (Min and Boff, 2002). On the other hand, tocopherols, tocotrienols and β-carotene may decrease oxidation reaction. Tocopherols and β-carotene act as quenchers of singlet oxygen (Choe and Min, 2006, 2009), while tocotrienols have an antioxidative activities in auto-oxidation (Kim, 2014).

Light intensity triggers photo-oxidation in food containing photosensitizers and influencing its nutritional quality (Min and Boff, 2002; Choe and Min, 2009). Several studies have shown the effect of light intensity on vegetable oil deterioration (Rahmani and Scallany, 1998; Psomiadou and Tsimidou, 2002; Rukmini and Raharjo, 2010; Kim and Choe, 2012, 2013; Choe, 2013). Even though RPO might be exposed to light during its storage and distribution, photo-oxidative stability of RPO has not been

*Corresponding author.
Email: *andarwulan@yahoo.com*

reported yet. Hence, the objective of this study was to investigate the effect of light intensities on minor compounds (chlorophyll, total tocopherol, carotene) and oxidative stability (peroxide, p-anisidine and total oxidation values) of RPO.

Materials and Methods

Materials

Crude Palm Oil (CPO) was obtained from Salim Ivomas Pratama Inc., Indonesia. α-Tocopherol standard was purchased from Sigma-Aldrich Chemical Co. (St Louis, MO, USA). N-hexane, isooctane, methylene chloride, toluene, 2,2 bipyridine, $FeCl_3.6H_2O$ and ethanol were purchased from J.T. Baker (Phillipsburg, NJ, USA). All chemicals used were of analytical grade.

Production of red palm oil (RPO)

Refinery processes from CPO to RPO included degumming, deacidification, deodorisation and fractionation. Degumming and deacidification processes were conducted according to Widarta *et al.* (2012). Degumming process was started by heating 60 kg of CPO at 80°C in a neutralisation tank. A solution of 85% (w/w) phosphoric acid was added under constant agitation of 56 rpm for 15 min. After degumming, deacidification process was conducted by adding NaOH solution (16°Be with 17.5% excess) at 61±2°C under agitation for 26 min. Soap stock was removed by centrifugation at 3,000 rpm for 20 min. After soap separation, the oil was washed using hot water with oil to water ratio of 7:1 (w/w), ensuring that the oil was free of soap. The temperature of hot water was 5-8°C higher than the oil. The resultant oil was called neutralised degummed red palm oil (NDRPO).

Deodorisation process was conducted as a batch system according to Riyadi (2009). A total of 80-90 kg NDRPO was homogenised at 46±2°C for 10 min in a 100 L deodorisation tank. After homogenisation, NDRPO was heated to 140°C under vacuum condition (20 mmHg). Nitrogen gas was passed gradually at 20 L/h for 1 h into deodorisation tank.

After deodorisation process, deodorised neutralised degummed red palm oil (DNDRPO) was dry fractionated by heating 100 kg oil up to 70°C for 10 min in a fractionation tank, according to Mursalin *et al.* (2013). The oil obtained was cooled gradually until it reached a temperature of 20°C. Olein fraction of RPO was separated using filter press filtration (Fadhel Teknik Ltd., Bogor, Indonesia). Then, the oil was poured into amber bottles, passed with N_2 gas for 1-2 min and sealed. The bottles were kept at -20°C and stored prior for analysis.

Photo-oxidation of oil

Photo-oxidation of oil was performed according to AOCS recommended practice Cg 6-01 (AOCS, 2003) with modification on light intensity. Thirty mL of RPO was poured into a 100 mL transparent serum bottle (77% headspace). The bottle was tightly capped with rubber and sealed with plastic parafilm. The samples were placed in mirror glass box (60 x 50 x 30 cm) equipped with nine fluorescent cool white light 18 watts. The mirror glass box was placed in wooden box (70 cm x 60 x 50 cm) equipped with a thermocouple, heater and 4 blowers relayed on the bottom of the glass box. Samples were exposed to light on intensities of 5,000, 10,000 and 15,000 lux at 31°C for 7 d of storage. Controls in wrapped (dark control, DC) and unwrapped (normal light control, NLC) transparent serum bottles with aluminum foil were stored at room light intensity and temperature 31±2°C. The samples and controls were collected and analyzed every d in triplicate.

Analysis of oil

The minor compounds changes in oil were analyzed by Shimadzu UV-2450 spectrophotometer (Shimadzu Co., Tokyo, Japan). The chlorophyll content of the oil was determined using AOCS method Cc 13i-96 (AOCS, 2003). The absorbances of samples were measured at 670, 630 and 710 nm using CH_2Cl_2 as blank. Chlorophyll content was calculated as follows:

$$\text{Chlorophyll content (mg/kg oil)} = \frac{34.5 \times (A_{670} - 0.5 \times A_{630} - 0.5 \times A_{710})}{L} \quad (1)$$

where A = absorbance at each wavelength and L = cuvette thickness (mm).

Carotene content was determined using PORIM method (PORIM, 1995). Four mg of sample was dissolved with hexane and diluted into 10 mL volumetric flask. The solution was transferred into 1 cm quartz cuvette and the absorbance was measured at 446 nm against hexane. The carotene content of samples was expressed as mg β-carotene/kg oil (molar absorption coefficient was 1.40 x 10^5 L/mol/cm).

Total tocopherols (including tocotrienols) was determined according Wong *et al.* (1988). Samples were weighed accurately 40 mg and transferred into 10 mL volumetric flask, added 5 mL of toluene, 3.5 mL of 2,2 bipyridine (0.07% w/v in 95% ethanol), 0.5 mL of $FeCl_3.6H_2O$ (0.2% w/v in 95% ethanol) and diluted into 10 mL with 95% ethanol. Samples were shaken and allowed to stay for 10 min. The absorbance was measured at 520 nm. Total tocopherol content was calculated based on α-tocopherol standard curve in

the range of 250-2000 mg/kg.

The degree of oil oxidation (peroxide value (PV) and p-anisidine value (AV)) was evaluated according to the AOCS method Cd 8-53 and Cd 18-90 (AOCS, 2003). Meanwhile, total oxidation (Totox) value was calculated using following equation:

$$\text{Totox value} = 2PV + AV \quad (2)$$

The fatty acid composition of the oil was analyzed by gas chromatography after esterification with 14% BF_3 in methanol using AOCS method Ce 1-62 (AOCS, 2003). The instrument used was a Shimadzu GC-2100 gas chromatograph (Shimadzu Co., Tokyo, Japan) equipped with a flame ionization and column DB-23 (30 m x 0.25 mm, 0.25 µm thick). The temperatures of the oven, the injector and the detector were 230, 250 and 260°C, respectively. The nitrogen flow rate was 5 mL/min and the split ratio was 30:1. Each fatty acid in the chromatogram was identified by comparing the retention times with those of standard fatty acid methyl esters and quantified by the peak areas.

Statistical analysis

SPSS program version 16.0 (SPSS Inc., Chicago, IL, USA) was used for the statistical analysis of the data. Statistical analyses were performed by paired t-test for refining process, one-way ANOVA and Duncan's multiple range at the 5% significance level for photo-oxidation of RPO. A linear regression analysis was used to find correlation coefficients between the minor compounds changes and the degree of RPO photo-oxidation.

Results and Discussion

Chemical characteristics

Chemical characteristics of crude and red palm oil (RPO) used for this study are shown in Table 1. RPO processing caused a significant decrease ($p<0.05$) in chlorophyll content from 10.01 mg/kg in CPO to 4.36 mg/kg in RPO. The chlorophyll content in RPO was higher than that of virgin coconut oil (0.097-0.098 mg/kg), but lower than that of virgin olive oil (4.1-15.1 mg/kg) (Rahmani and Scallany, 1998; Psomiadou and Tsimidou, 2002; Rukmini and Raharjo, 2010). The chlorophyll content in virgin coconut and olive oil acted as photosensitizers (Rahmani and Scallany, 1998; Psomiadou and Tsimidou, 2002; Rukmini and Raharjo, 2010). Lee *et al.* (1997) reported that chlorophyll content in the range of 0.065-1.33 mg/kg in vegetable oil can initiate photo-oxidation reaction. One sensitizer molecule may generate 10^3 to 10^5 molecules of singlet oxygen before becoming inactive (Choe and Min, 2006). Even though chlorophyll may act as sensitizer, total tocopherol and carotene contents in RPO remained high, 96% and 97% of initial content, respectively. Tocopherols and carotene are reported to act as antioxidants during photo-oxidation (Choe and Min, 2006, 2009).

Table 1. Chemical characteristics of crude and red palm oil

Characteristics	Crude palm oil	Red palm oil
Chlorophyll (mg/kg)	10.01±0.05[a]	4.36±0.03[b]
Total tocopherol (mg/kg)	1174.20±29.58[a]	1127.49±19.50[a]
Carotene (mg/kg)	578.90±8.04[a]	559.39±4.26[a]
Peroxide value (mequiv/kg)	1.66±0.12[a]	0.84±0.06[b]
p-Anisidine value	7.46±0.10[a]	8.74±0.10[b]
Totox value	9.88±0.10[a]	10.35±0.12[b]

Notes: All data are the means±SD of three replicates. [a,b] Means in the same row within the grup with different letters are significantly different ($p<0.05$) (paired t-test)

RPO used for this study had low level of oxidation during processing, indicated by its low PV (Table 1). However, RPO processing caused a significant increase ($p<0.05$) in AV and Totox value of RPO. This result indicated that RPO processing can reduce peroxides but not aldehyde compounds. Aldehyde compounds are products of peroxides decomposition.

Major fatty acids of RPO consisted of palmitic (35.8% w/w), stearic (3.9% w/w), oleic (40.3% w/w) and linoleic acid (11.0% w/w) with saturated/unsaturated fatty acids ratio of 45:55. Consequently, RPO was thought to be susceptible to photo-oxidation, due to rich electron in double bonds of unsaturated fatty acids (Min and Boff, 2002).

Minor compounds changes during photo-oxidation

The effect of light intensities on chlorophyll, total tocopherol and carotene contents in RPO during 7 d of storage are shown in Figure 1a, 1b and 1c. The changes of chlorophyll content in the samples stored in light were higher than that stored in the dark (Figure 1a). Chlorophyll content of RPO under normal light storage (normal light control, NLC) decreased 21.86% (2.47 mg/kg); while under dark storage (dark control, DC) decreased 1.47% (3.12 mg/kg) after 7 d of storage. Exposure to light on intensities of 5,000, 10,000 and 15,000 lux sharply decreased the chlorophyll content of RPO 23.60% (2.87 mg/kg), 24.55% (2.81 mg/kg) and 30.92% (2.68 mg/kg) within 12 h of storage, respectively. This finding might be related to the high-light-intensity that supplies more energy to exitate the chlorophyll and accelerate its degradation.

Rapid depletion of chlorophyll at the first 12 h of light exposure can be explained in term of singlet

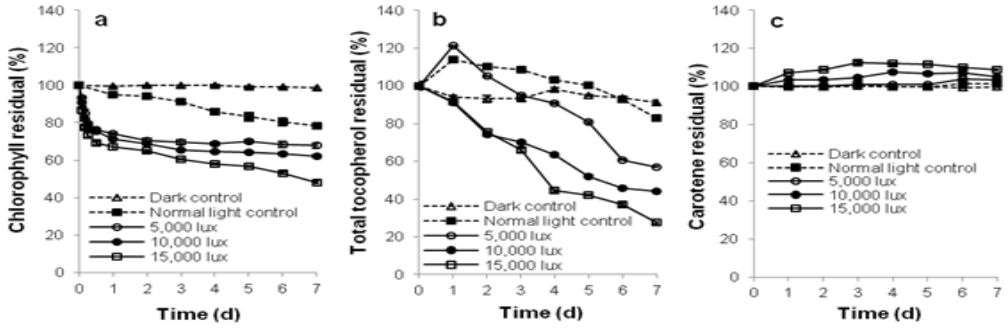

Figure 1. Effect of light intensities on (a) chlorophyll, (b) total tocopherol and (c) carotene contents in RPO during storage. Controls are samples that were stored in dark and normal light storage. Error bars represent standard error of the mean (n=3)

oxygen formation. According to Min and Boff (2002), exposure to light can cause chlorophyll to excite and act as a photosensitizer type II that react with triplet oxygen to form highly reactive singlet oxygen. Singlet oxygen directly attacks double bond between fifth and sixth carbon of chlorophyll-a, resulting in a subsequent shift of the position of the double bond and formation of hydro-peroxides, which are then further cleaved through oxygen-oxygen linkage and form degradation products (Chen and Huang, 1998). Figure 1a shows that the degradation of chlorophyll slowed down after 12 h. Chlorophyll content in RPO after 7 d of storage under light intensities of 5,000 and 10,000 lux decreased 32.18% (2.55 mg/kg) and 37.90% (2.31 mg/kg), respectively, which were significantly lower ($p<0.05$) than that of 15,000 lux (51.87%, 1.87 mg/kg). The slowing down of degradation of chlorophyll probably associated with the activity of carotene and tocopherol against photo-oxidation in RPO. Carotene quenches singlet oxygen or triplet sensitizer excited via energy transfer, while tocopherol quenches singlet oxygen via electron transfer and scavenges peroxy or alkyl radicals (Choe and Min, 2006, 2009).

In case of total tocopherol, exposure to light resulted in changes of its content in RPO. Figure 1b shows that the total tocopherol content in DC decreased slowly during 7 d of storage. However, in NLC and 5,000 lux exposed samples it decreased after 1 d of storage. Figure 1b indicates unlikely increase of total tocopherol in the first d of light exposure. The unlikely increase of total tocopherol was probably due to the formation of tocopheroxyl radical which have higher molar extinction coefficient than tocopherol in the UV-vis spectrum (Kohno *et al*., 2011; Mukai *et al*., 2012). Prolonged exposure, however, showed a decrease in the total tocopherol. Exposure to light on intensities of 5,000, 10,000 and 15,000 lux triggered more rapid decrease of total tocopherol than that of NLC sample. The phenomenon of tocopherol absorption increase was not observed in the exposure to light on intensities of 10,000 and 15,000 lux which associated with rapid decrease of the total tocopherol.

Similar to that observed in chlorophyll, increase in light intensity accelerated total tocopherol degradation ($p<0.05$). When RPO samples were exposed to light on intensities of 5,000, 10,000 and 15,000 lux, total tocopherol content decreased 43.04% (605.14 mg/kg), 56.06% (580.85 mg/kg) and 72.57% (292.66 mg/kg) after 7 d of storage, respectively. While, the total tocopherol content of DC decreased 8.69% (983.04 mg/kg) which was lower ($p<0.05$) than NLC (17.28%, 888.00 mg/kg) after 7 d of storage. High-light-intensity supplied more energy to produce singlet oxygen for further progression of oxidation. Degradation of total tocopherol during photo-oxidation was due to its chemical quenching of singlet oxygen and free-radical scavenging, while degradation of total tocopherol in auto-oxidation (dark) was due to its free-radical scavenging (Choe and Min, 2006, 2009). Sabliov *et al.* (2009) suggested that the degradation of α-tocopherol dissolved in hexane and methanol under UV light occurred via oxidation by superoxide anion radicals generated under light and hydroperoxy radicals converted from superoxide anion radicals, resulting in the tocopheroxy radical. Light also supplies the energy to break the O–H bond and ether linkage in the tocopherol structure, resulting in the semiquinone radical and then quinones (Sabliov *et al*., 2009).

On the other hand, there was no significant changes on carotene content in RPO ($p>0.05$) during 7 d of storage under dark or exposure to light (Figure 1c). The high stability of carotene content during storage was probably due to the presence of tocopherols and tocotrienols in RPO. According to Yi *et al.* (2011), a slight decrease of carotene in RPO during auto-oxidation was associated with regeneration of carotene by tocopherols or tocotrienols. Schroeder *et al*. (2006) and Rossi *et al*. (2007) also noted that

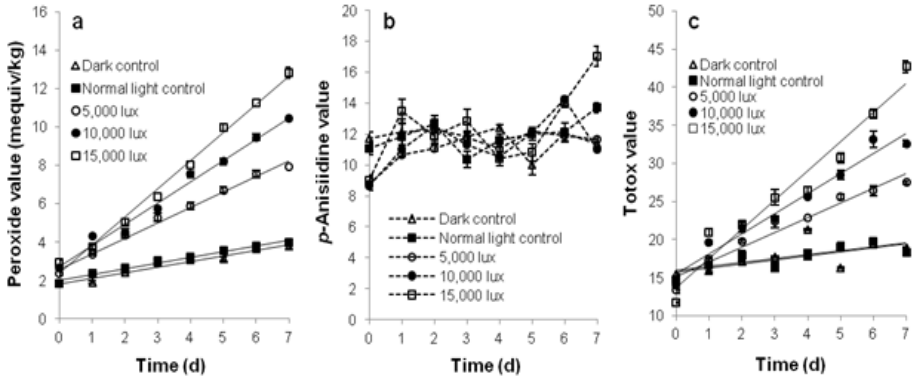

Figure 2. Effect of light intensities on (a) peroxide value, (b) p-anisidine value and (c) Totox value in RPO during storage. Controls are samples that were stored in dark and normal light storage. Error bars represent standard error of the mean (n=3)

between tocopherols, tocotrienol and β-carotene showed a synergistic antioxidant activity during thermal oxidation. However, this study did not investigate the interaction between tocopherols, tocotrienol and β-carotene in RPO during photo-oxidation.

Photo-oxidative stability of RPO

The effect of light intensities during storage on PV in RPO is shown in Figure 2a. Exposure to high-light-intensity directly increased peroxide formation in RPO ($p<0.05$). PV in DC, NLC, intensities of 5,000, 10,000 and 15,000 lux exposed samples increased from 1.83, 1.83, 2.38, 2.67, 2.81 to 3.79, 3.96, 7.92, 10.01 and 12.84 mequiv/kg after 7 d of storage, respectively. This result indicated that the light exposure with relatively high intensity was very effective at initiating photo-oxidation. Oil oxidation is accelerated by light, especially in the presence of sensitizers such as chlorophylls.

As can be seen on Figure 2a, the increase of PV can be explained by zero order reaction kinetics, at which exposure to light under intensities of 5,000, 10,000 and 15,000 lux proportionally increased the reaction rate constant (k value) to 0.806 (r^2 = 0.99), 1.107 (r^2 = 0.99) and 1.468 mequiv/kg/d (r^2 = 0.99) in RPO, respectively. Exposure to high-light-intensity accelerated the chlorophyll excitation and transferred more energy onto adjacent triplet oxygen to form active singlet oxygen (Min and Boff, 2002). Electrophilic singlet oxygen directly react with high-electron-density of double bonds producing both conjugate and non-conjugate hydro-peroxides (Min and Boff, 2002; Choe and Min, 2006; Rukmini and Raharjo, 2010). The quantity of hydro-peroxides formed during photo-oxidation was proportional to the amount of light absorbed (Chen and Huang, 1998; Rukmini and Raharjo, 2010).

AV indicated the number of aldehyde compounds which are secondary oxidation products of peroxides decomposition. Light exposure to RPO caused no significant changes ($p>0.05$) in AV as shown in Figure 2b. The insignificant changes of AV were likely due to the lack of peroxides degradation and AV only measured 2-alkenal and 2,4-dienal which were not significantly correlated to nonanal (Tompkins and Perkin, 1999; AOCS, 2003). Nonanal is the selected aldehyde that would be primarily formed by the breakdown of oleic acid (Tompkins and Perkin, 1999). Furthermore, aldehydes were unstable carbonyl compounds which were easily decomposed or transformed into another compounds. The insignificant changes of AV were also reported in oxidation of soy oil and conjugated linoleic acid rich soy oil (Yettela *et al.*, 2012).

Figure 2c shows that Totox value of controls in DC and NLC increased slightly during 7 d of storage. The Totox value in RPO showed a linear increase ($p<0.05$) during high-light-intensity storage. The linear increase of Totox value followed zero order reaction kinetics with k values 1.93 (r^2 = 0.95), 2.63 (r^2 = 0.96) and 3.83 per d (r2 = 0.95) on the intensities of 5,000, 10,000 and 15,000 lux, respectively. The increasing pattern of Totox value was similar to PV especially on exposure to light with the intensities of 5,000, 10,000 and 15,000 lux.

Relationship between the minor compounds changes and photo-oxidative stability of RPO

Relationship between the minor components changes and photo-oxidative stability of RPO are shown in Figure 3. The effect of light intensities during photo-oxidation was evaluated by correcting the light-storage-experimental-data. The experimental data was corrected by reducing the light storage data (LC, 5,000, 10,000 and 15,0000 lux) with the dark storage data (DC) (Figure 3a, 3b, 3c and 3d).

Figure 3a, 3b, 3c and 3d show that the chlorophyll

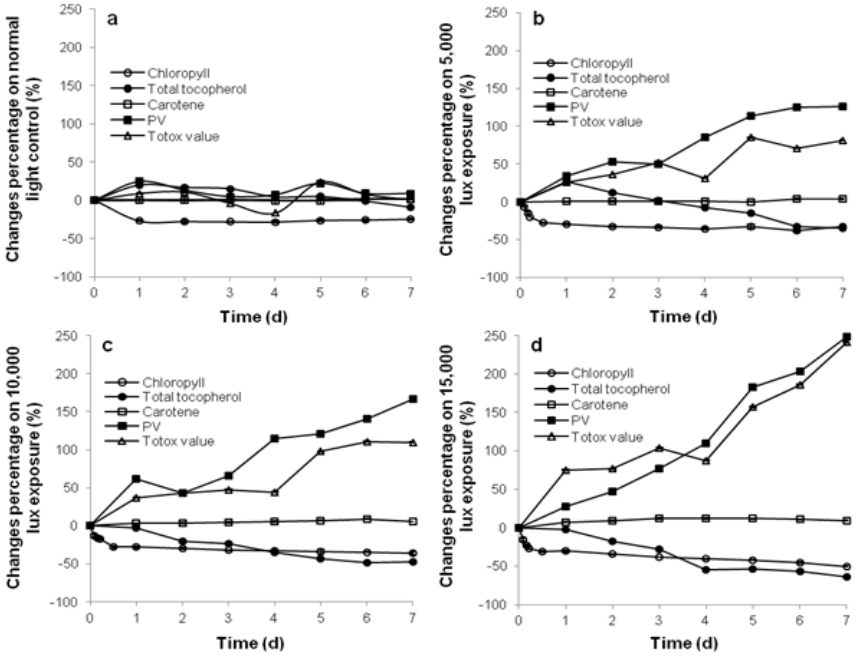

Figure 3. The minor components changes and stability of RPO during storage on (a) normal light control, (b) intensities of 5,000 lux, (c) 10,000 lux and (d) 15,000 lux. Error bars represent standard error of the mean (n=3)

decreased at early stage of light treatments and the total tocopherol directly decreased only on light intensities of 10,000 and 15,000 lux, while the carotene remained at all treatments. Chlorophyll absorbs energy from the light and results in the formation of singlet oxygen (Min and Boff, 2002). The singlet oxygen oxidizes the electron-rich-double-bond in chlorophyll and fatty acid to form peroxides and hydro-peroxides (Min and Boff, 2002; Choe and Min, 2006; Rukmini and Raharjo, 2010). Therefore, exposure to light decreased ($p<0.05$) chlorophyll along with an increase in PV and Totox value at early stage of photo-oxidation. However, since the exposure to light on NLC was low (approximately 476.25±15.27 lux for 35 hours a week), PV and AV were not significantly increased ($p>0.05$) while the total tocopherol remained constant.

As shown in Figure 3b, the increase in PV and AV activated tocopherol as antioxidant. However, there was an increase ($p<0.05$) of total tocopherol on the first d under light intensity of 5,000 lux which was followed by degradation in the following d. This phenomenon was probably due to tocopheroxyl radical formation (Kohno *et al*., 2011; Mukai *et al.*, 2012) during initial photo-oxidation of tocopherol. Meanwhile PV and AV consistently increased ($p<0.05$) during 7 d of storage, total tocopherol decreased after 3 d of storage.

As shown in Figure 3c and 3d, the increase of PV and AV on light intensities of 10,000 and 15,000 lux was followed by a direct decrease of total tocopherol.

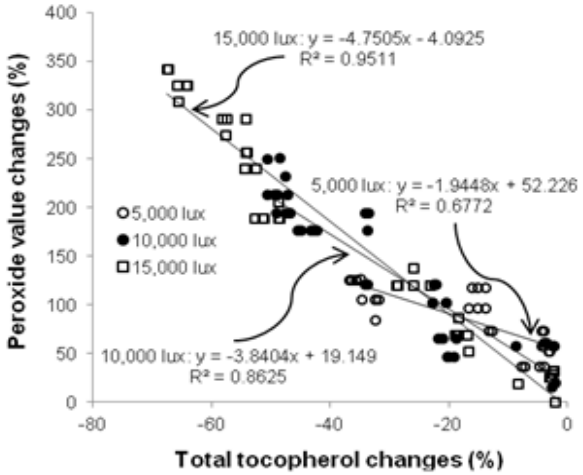

Figure 4. Correlation between peroxide value and total tocopherol changes in RPO during storage under different light intensities

As primary product of oxidation, PV increased faster than that of Totox value on light intensities up to 10,000 lux. However, Totox value increased faster than PV on the early stage of 15,000 lux which indicated that further oxidation has occurred at this stage.

Exposure to light on intensities of 5,000, 10,000 and 15,000 lux accelerated the increase of PV and decreased total tocopherol content in RPO, as shown in Figure 3b, 3c and 3d, respectively. The relationship between PV and total tocopherol changes showed negative linear equations (Figure 4). The negative sign of slope in the regression equations indicates that the more the oil was oxidized, the lower was

the tocopherol content and thus the higher was the tocopherol degradation. The slope indicates the degree of dependence of RPO oxidation on the tocopherol content. The slope and r^2 ($0.68<r2<0.95$) increased as the light intensity increased during storage, indicating the higher dependence on the tocopherol content and correlation. Since the effect of light intensity during storage associated with the amount of light energy exposure, light increased the dependence of RPO oxidation on tocopherol content during storage. The light increased the dependence of lipid oxidation on tocopherol content was also reported during storage of diacylglycerol-rich oil derived from olive and perilla oil and sunflower oil (Kim and Choe, 2012; Choe 2013).

Conclusion

Photo-oxidation of chlorophyll and total tocopherol in RPO has been observed during 7 d of storage in which their degradation were proportional to the light intensity. However, photo-oxidation was not observed on carotene. Photo-oxidation was also indicated by the increase of PV and Totox value. Their increase rates were higher at higher light intensity which can be described using zero order kinetic model. A significant negative correlation between PV and total tocopherol changes was also found. PV was more sensitive to the changes of total tocopherol at higher light intensity. This result suggests that the light intensity increased the dependence of lipid oxidation on tocopherol content during storage of RPO.

Acknowledgment

We would like to thank the Directorate General of Higher Education, the Ministry of National Education the Republic of Indonesia for the financial support through the Doctorate Research Grant in 2014.

References

AOCS. 2003. Official Methods and Recommended Practices of the American Oil Chemists' Society. 2th ed. Champaign: American Oil Chemist's Society Press.

Chen, B. H. and Huang, J. H. 1998. Degradation and isomerization of chlorophyll a and β-carotene as affected by various heating and illumination treatments. Food Chemistry 62(3): 299-307.

Choe, E. and Min, D. B. 2006. Mechanisms and factors for edible oil oxidation. Comprehensive Reviews in Food Science and Food Safety 5: 169-86.

Choe, E. and Min, D. B. 2009. Mechanisms of antioxidants in the oxidation of foods. Comprehensive Reviews in Food Science and Food Safety 8: 345–358.

Choe, E. 2013. Interaction of light and temperature on tocopherols during oxidation of sunflower oil. Journal of the American Oil Chemists' Society 90(12): 1851-857.

Dauqan, E., Sani, H. A., Abdullah, A., Muhammad, H. and Top, A. G. M. 2011. Vitamin E and beta carotene composition in four different vegetable oils. American Journal of Applied Sciences 8(5): 407-412.

Idris, C. A. C., Karupaiah, T., Sundram, K., Tan, Y. A., Balasundram, N., Leow, S. S., Nasruddin, N. S. and Sambanthamurthi, R. 2014. Oil palm phenolics and vitamin E reduce atherosclerosis in rabbits. Journal of Functional Food 7: 541-550.

Kim, N. and Choe, E. 2012. Singlet oxygen-related photooxidative stability and antioxidant changes of diacylglycerol-rich oil derived from mixture of olive and perilla oil. Journal of Food Science 77(11): C1185- C1191.

Kim, N. and Choe, E. 2013. Contribution of minor compound to the singlet oxygen-related photo-oxidation of olive and perilla oil blend. Food Science and Biotechnology 22(2): 315-321.

Kim, H. J. 2014. Effect of α-, β-, γ- and δ-tocotrienol on the oxidative stability of lard. Journal of the American Oil Chemists' Society 91(5): 777-782.

Kohno, Y., Fujii, M., Matsuoka, C., Hashimoto H., Ouchi A., Nagaoka S. and Mukai K. 2011. Notable effects of the metal salts on the formation and decay reactions of α-tocopheroxyl radical in acetonitrile solution. The complex formation between α-tocoperoxyl and metal cations. The Journal of Physical Chemistry B 115: 9880-9888.

Lee, K. H., Jung, M. Y. and Kim, S. Y. 1997. Quenching mechanism and kinetics of ascorbyl palmitate for the reduction of photosensitized oxidation of oils. Journal of the American Oil Chemists' Society 74(9): 1053-1057.

Mba, O. I., Dumont, M. J. and Ngadi, M. 2015. Palm oil: Processing, characterization and utilization in the food industry – A review. Food Bioscience 10: 26-41.

Min, D. B. and Boff, J. 2002. Chemistry and reaction of singlet oxygen in foods. Comprehensive Reviews in Food Science and Food Safety 1: 58-72.

Mukai, K., Kohno, Y., Ouchi, A. and Nagaoka, S. 2012. Notable effects of metal salts UV-Vis absorption spectra of α-, β-, γ- and δ-tocopheroxyl radicals in acetonotrile solution. The complex formation between tocopheroxyls and metal cations. The Journal of Physical Chemistry B 116: 8930-8941.

Mukherjee, S. and Mitra, A. 2009. Health effects of palm oil. Journal of Human Ecology 26(3): 197-203.

Mursalin, Hariyadi, P., Purnomo, E. H., Andarwulan, N. and Fardiaz, D. 2013. Fraksinasi kering minyak kelapa menggunakan kristalisator skala 120 kg untuk menghasilkan fraksi minyak kaya triasilgliserol rantai menengah. Jurnal Penelitian Tanaman Industri 19: 41-49.

PORIM. 1995. PORIM Test Method, p. 2.6. Kuala Lumpur: Ministry of Primary Industries of Malaysia.

Psomiadou, E. and Tsimidou, M. 2002. Stability of virgin olive oil. 2 Photo-oxidation studies. Journal of Agricultural and Food Chemistry 50(4): 722-727.

Rahmani, M. and Scallany, A. S. 1998. Role of minor constituents in the photooxidation of virgin olive oil. Journal of the American Oil Chemists' Society 75(7): 837-843.

Rice, L. and Burns, J. B. 2010. Moving from efficacy to effectiveness: Red palm oil's role in preventing vitamin A deficiency. Journal of the American College of Nutrition 29(3): 302S-313S.

Riyadi, A. H. 2009. Kendali proses deodorisasi dalam permurnian minyak sawit merah skala pilot plant. Bogor, Indonesia: Bogor Agricultural University, MSc thesis.

Rossi, M., Alamprese, C. and Ratti S. 2007. Tocopherols and tocotrienols as free radical-scavengers in refined vegetable oils and their stability during deep-fat frying. Food Chemistry 102(3): 812-817.

Rukmini, A. and Raharjo, S. 2010. Pattern of peroxide value changes in virgin coconut oil (VCO) due to photo-oxidation sensitized by chlorophyll. Journal of the American Oil Chemists' Society 87: 1407-1412.

Sabliov, C. M., Fronczek, C., Astete, C.E., Khachaturyan, M., Khachatryan, L. and Leonardi, C. 2009. Effects of temperature and UV light on degradation of α-tocopherol in free and dissolved form. Journal of the American Oil Chemists' Society 86: 895–902.

Sambanthamurthi, R., Sundram, K. and Tan, Y. A. 2000. Chemistry and biochemistry of palm oil. Progress in Lipid Research 39: 507-558.

Schroeder, M. T., Becker, E. M. and Skibsted, L. H. 2006. Moleculer mechanism of antioxidant synergism of tocotrienols and carotenoids in palm oil. Journal of Agricultural and Food Chemistry 54(9): 3445-3453.

Tompkins, C. and Perkin, E. G. 1999. The evaluation of frying oils with the p-anisidine value. Journal of the American Oil Chemists' Society 76(8): 945-947.

Usuki, R., Usuki, T., Endo, Y. and Kande, T. 1984. Residual amounts of chlorophylls and pheophytins in refined edible oils. Journal of the American Oil Chemists' Society 61(4): 785-788.

Widarta, I. W. R., Andarwulan, N. and Haryati, T. 2012. Optimasi proses deasidifikasi dalam pemurnian minyak sawit merah skala pilot plant. Jurnal Teknologi dan Industri Pangan 23: 41-46.

Wong, M. L., Timms, R. E. and Goh, E. M. 1988. Colorimetric determination of total tocopherols in palm oil, olein and stearin. Journal of the American Oil Chemists' Society 65(2): 258-261.

Yettela, R. R., Castrodale, C. and Proctor, A. 2012. Oxidative stability of conjugated linoleic acid rich soy oil. Journal of the American Oil Chemists' Society 89(4): 685-693.

Yi, J., Andersen, M. L. and Skibsted, L. H. 2011. Interactions between tocopherols, tocotrienol and carotenoids during autoxidation of mixed palm olein and fish oil. Food Chemistry 127(4):1792-1797.