The Effect of Bleaching and Physical Refining on Color and Minor Components of Palm Oil

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ABSTRACT: An industrially degummed Indonesian palm oil was bleached and steam refined in a pilot plant to study the effect of processing on oil color and on the levels of carotenoids and tocopherols. Five concentrations of one natural and two activated clays mixed with a fixed amount of synthetic silica were used for bleaching. For color measurement, the Lovibond method was compared to the CIE (Commission Internationale de l'Eclairage) L*, a*, b* method. The results showed that the L*, a*, b* method is repeatable and that the values found are highly correlated with the carotenoid content of bleached oil samples. The various clays and synthetic silica mixes removed 20–50% of the carotenoids in the degummed oil, depending on clay concentration and activity. For the two activated clays, pigment adsorption increased with clay amount. Steam refining totally destroyed carotenoids in the clay-treated oils by heat bleaching. Total tocopherols in the crude oil amounted to 1000 mg/kg, with γ-tocotrienol as the main tocopherolic component followed by α-tocopherol, α-tocotrienol, and δ-tocotrienol. Tocopherol concentrations increased after the bleaching treatment with the most acid clay, and the increase was proportional to the amount of clay used. Both bleaching and steam refining changed the ratios between the various tocopherolic components, especially increasing the relative concentration of α-tocotrienol in the refined oil. An average 80% tocopherol retention was obtained after the treatment with acid clay + synthetic silica and steam refining of palm oil.

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KEY WORDS: Bleaching, carotenoids, color, palm oil, physical refining, tocopherols.

Crude palm oil contains about 500–700 mg/kg of carotenoids, mainly α- and β-carotene, and 600–1000 mg/kg of tocopherols (1), such as tocols and tocotrienols. These compounds are all involved in health maintenance, since carotenoids are vitamin A precursors and tocopherols can prevent or minimize free radical damage associated with cancer, cardiovascular disease, premature aging, cataracts, air pollution, and strenuous exercise (2).

A refining process must be applied to crude oil to obtain the purity characteristics (acidity, color, etc.) desirable in an edible oil (3).

Crude palm oil is generally refined by the physical process, which includes a degumming pretreatment, a bleaching step, and a high-temperature (240–260°C), low-pressure (1–3 mm Hg) deodorization/deacidification step. Physical refining is preferred to the chemical process since the high acidity that is frequently observed in crude palm oil (up to 5%) can lead to excessive loss of neutral oil in the soapstock after alkali neutralization. Moreover, the high temperature reached during the deodorization/deacidification step should positively contribute to the bleaching of the oil (heat bleaching).

The volatility of tocopherols ranges between the high levels observed in free fatty acids and the relatively low levels of triacylglycerols (4). During physical refining, tocopherols are partially steam stripped, their level being reduced to 356–630 mg/kg in refined palm oil (1).

When assessing operative conditions for physical refining, it is important to find a compromise between the need to maximize the heat bleaching of carotenoids and the desire to minimize the stripping of tocopherols, thus improving the stability of the finished oil. The possibility of using mild process conditions is, however, dependent on the quality of crude oil, in particular on its acidity, which in any case must be lowered below 0.1% in refined, bleached, and deodorized (RBD) palm oil (3). In order to improve the quality of refined oil, De Greyt (5) suggests a two-step deodorization, which includes a first step under mild temperature conditions and a further step at a higher temperature for a shorter time.

Physically refined palm oil is a very light golden yellow and contains essentially no carotenoids. Since the world production of refined palm oil amounts to about 20×10^6 tons (6), every year 1.2×10^4 tons of carotenoids are destroyed. However, by means of low-temperature and low-pressure molecular distillation, it is possible to produce a refined red palm oil still rich in both carotenoids and tocopherols (7).

The Lovibond method is widely used in the oil industry to assess the color of oil. The method, which consists of visually matching the color of the melted fat with red and yellow Lovibond color glasses (8), is definitely subjective, being dependent on the chromatic capacity of the observer.

The aim of the present work was (i) to test an objective method for color measurement [CIE (Commission Internationale de l'Eclairage) L*, a*, b*], comparing it to the Lovibond system, and (ii) to study the effect of bleaching and physical refining on palm oil color and on its content of carotenoids and tocopherols.

EXPERIMENTAL PROCEDURES

Materials. Indonesian crude palm oil (5.02% free fatty acids) was used for the experiments. After acid degumming in an in-

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dustrial plant, 10-kg oil batches were treated in a pilot plant consisting of a bleaching vessel and a steam physical refining vessel (9). Operative conditions were 110°C for 20 min under vacuum (70–80 mm Hg) for bleaching, and 250°C for 2.5 h at 2–3 mm Hg for physical refining.

Five concentrations (from 0.5 to 1.0% of the oil mass) of one natural and two activated clays mixed with 0.125% (of the oil mass) synthetic silica were used for bleaching, thus obtaining 15 samples of bleached oil and as many bleached, steam-refined oil samples (from now on called RBD or refined samples). Table 1 reports the characteristics of the adsorbents used.

Lovibond color. A Lovibond tintometer was used, and the color of oil was matched with a set of standard colored, numbered glasses, ranging in the scales from 0 to 70 red (R) and 0 to 70 yellow (Y). A 1-in. vessel was used for crude and degummed oil color measurements, and a 5.25-in. vessel was used for bleached and refined oils. Before the measurements, oil samples were melted at 45°C. Results are expressed as R and Y values.

CIE L, a*, b* color.* A Minolta CT-310 colorimeter (Minolta Co., Ltd., Osaka, Japan) for transmittance color measurements in liquid media was used. Results are expressed as L*, a*, b*, respectively, corresponding to lightness, the green–red component, and the blue–yellow component. The hue value (a*/b*) was also calculated. Before the measurements, the instrument was calibrated with deionized water. Measurements were performed on melted samples (45°C) placed in a 20-mm tube. Results are the average of three consecutive measurements.

Total carotene. For total carotene analysis, oil samples were suitably diluted in isooctane and their absorbance at 450 nm was assessed using a PerkinElmer Lambda 3 spectrophotometer (PerkinElmer Co., Norwalk, CT). Results were expressed as β-carotene equivalents after comparison with a calibration curve prepared with β-carotene (Merck, Darmstadt, Germany) solutions in isooctane ranging from 0 to 5 mg/L. Sample spectra were also scanned between 380 and 500 nm at 120 nm/min.

Tocopherols. Oil samples were diluted with hexane and filtered through a 0.22 µm GV membrane (Millipore Co., Bedford, MA). A dilution ratio of 1:50 (wt/vol) was used for crude or bleached oils, and a ratio of 1:12.5 (wt/vol) was used for refined oils. A normal-phase high-performance liquid chromatography (HPLC) analysis was performed following the analytical conditions reported by Dionisi *et al.* (10). HPLC equipment included a Jasco PU-980 pump (Jasco Co., Tokyo, Japan), a Reodyne injector mounting a 50 µL loop, a variable wavelength detector UV Lambda Max 486 (Waters Co., Milford, MA), a µ-Porasil 3.9- × 300-mm column (Waters) equipped with a Lichrocart SI 60 cartridge (Merck) as precolumn, and a D-2000 Chromato-Integrator (Merck-Hitachi, Darmstadt, Germany). Operative conditions were as follows: mobile phase, 0.3% 2-propanol in hexane (all HPLC grade, Merck); flow rate, 1.7 mL/min; wavelength, 290 nm. Calibration curves were prepared for the most representative tocopherolic components of palm oil by analyzing standard solutions in hexane of the following: α-tocopherol (Merck), ranging from 2 to 7 mg/L; α-tocotrienol (Merck), ranging from 5 to 20 mg/L; γ-tocotrienol (Merck), ranging from 5 to 40 mg/L; δ-tocotrienol (Merck), ranging from 2.5 to 17.7 mg/L. Total tocopherol concentration in crude oil, including nonidentified peaks, was evaluated by calculating an average response factor (based on the available standards) and applying it to the nonidentified peaks of the chromatogram.

TABLE 1
Properties of Utilized Adsorbents

Code	Type	pH[a]
C1	Activated clay	2.5
C2	Activated clay	3.2
C3	Natural clay	6–7
S	Synthetic silica	4.5

[a] Measured in a 5% water dispersion.

RESULTS AND DISCUSSION

The repeatability of color measurements was evaluated by means of a Minolta CT-310 colorimeter on 10 replicated readings of an industrially bleached palm oil. For each replicate the oil sample in the measuring tube was changed. The average L*, a*, b* values were 67.07 [standard deviation (SD) = 0.09], 47.05 (SD = 0.07), and 114.93 (SD = 0.12), respectively, with coefficients of variation of 0.13, 0.15, and 0.10%. The coefficients of variation obtained indicate the excellent repeatability of the method.

Table 2 shows total carotene concentrations and the color measurements, according to the Lovibond (Y, R) and the CIE (L*, a*, b*) methods, of crude and degummed palm oil, and of samples bleached using different clays. The various clays + synthetic silica mixes remove 20–50% of the carotenoids in the degummed oil, depending on the kind of clay used and on its concentration. The most acid activated clay (C1) adsorbs more pigments than the other clays. Considering the two activated clays, pigment adsorption increases with clay concentration.

Except for the Y values, all color parameters in the bleached samples are correlated ($P < 0.001$) with the residue levels of carotenoids. The correlation coefficients (Table 3) differ among color parameters, however, with Lovibond R showing the lowest r value.

Palm oil color is essentially due to carotenoid pigments. Actually, by using the Lovibond scale, a correlation with carotenoids is observed only with the red component R; while using the L*, a*, b* method, a correlation with all the color components can be found. The L*, a*, b* method seems more suitable then for describing the complexity of palm oil color.

Table 4 reports the color values of refined oils. A constancy in the color of RBD palm oil samples was observed, for the hue values (a*/b*) in particular.

Carotenoid levels in the finished oils were not quantifiable because, considering the absorbance spectrum of a RBD palm oil, the characteristic carotenoids peaks around 450 nm were not present (Fig. 1). Instead, a background absorbance, not

TABLE 2
Carotenoid Content and Color Evaluation in Lovibond (Y, R) and CIE (L*, a*, b*) Units in Crude, Degummed, and Bleached Palm Oil Samples[a]

	Carotenoids	Lovibond		CIE			
Palm oil	(mg/kg)	Y	R	L*	a*	b*	a*/b*
Crude	455.75	8	18	39.09	47.35	67.26	0.70
Degummed	415.00	8	17	47.91	51.42	82.57	0.62
Bleached with C1 + 0.125% S							
0.5%	297.09	14	13	63.77	54.34	109.89	0.49
0.625%	275.57	13	12	65.61	52.55	113.13	0.46
0.75%	245.84	10	12	67.31	50.47	116.03	0.43
0.875%	215.30	10	11	69.15	47.46	118.44	0.40
1.00%	223.43	11	11	69.51	47.39	119.06	0.40
Bleached with C2 + 0.125% S							
0.5%	327.92	12	12	62.75	54.55	108.20	0.50
0.625%	315.39	8	13	63.20	54.02	108.94	0.50
0.75%	313.95	9	13	64.43	52.84	111.03	0.48
0.875%	267.60	10	11	65.94	50.69	113.64	0.45
1.00%	258.60	10	11	67.08	49.28	115.67	0.43
Bleached with C3 + 0.125% S							
0.5%	324.41	7	14	59.74	58.95	103.01	0.57
0.625%	331.45	8	16	60.39	58.51	104.07	0.56
0.75%	329.91	10	14	60.86	58.53	104.90	0.56
0.875%	326.81	8	14	61.15	58.13	105.37	0.55
1.00%	304.01	8	14	61.44	57.79	105.91	0.55

[a] Y, Lovibond yellow; R, Lovibond red; CIE, Commission Internationale de l'Eclairage; L*, lightness; a*, green–red; b*, blue–yellow; a*/b*, hue value.

dependent on the wavelength, was observed. Thus, carotenoids are totally removed by heat bleaching during steam refining. Actually, the purpose of clay bleaching during palm oil processing is only in part the removal of pigments, since this purpose is better attained by steam refining. Rather the role of clays is to remove other nonvolatile compounds, which are dangerous for the stability of the finished oil (i.e., metals and phosphorus) and which, if they are present during steam refining (i.e., phosphorus), can cause foaming and the formation of degradation products.

Table 5 reports the levels of the main tocopherols detectable in crude palm oil and bleached oil samples treated with the most acid clay (C1). α-Tocopherol and α-, γ-, and δ-tocotrienols were the identified compounds.

Total tocopherols in crude oil, including nonidentified peaks, amounted to 1000 mg/kg and are consistent with the level reported by Goh *et al.* (1). The main tocopherol identified was γ-tocotrienol, which is also the tocopherolic compound with the highest antioxidant activity (11,12).

Table 5 shows that the total quantity of the identified tocopherols increased after bleaching with the acid clay + synthetic silica mix, and such increases were proportional to the percentage of clay used. Excluding the value corresponding to a clay concentration of 0.875%, a significant linear positive correlation ($r = 0.999$; $P < 0.001$) was found between the clay concentration and the summed tocopherols. This result confirms the observation of Gapor *et al.* (13), who found a tocopherol increase in bleached oils. The authors ascribed the phenomenon to the regeneration of the free form from dimeric or other esterified compounds. We can assume that, owing to its acidity, clay causes the release of tocopherols from the linked forms in proportion to clay concentration. Since the antioxidant activity of tocopherols is related to the presence of the free OH group in the molecule (14), it is possible to say that the acid clay treatment of palm oil increases the oil antioxidant content. However, the releasing effect is not indiscriminate, and γ-tocotrienol is partially destroyed by the treatment. In fact, the data reported in Table 5 show that bleaching caused an increase in the relative concentrations of α-tocopherol and α-tocotrienol while lowering γ-tocotrienol levels.

TABLE 3
Correlation Coefficients (*r*) and Correlation Probability (*P*) of Color Parameters and Residual Carotenoid Content in Palm Oil Samples Bleached with Clays and Synthetic Silica

	Y	R	L*	a*	b*	a*/b*
r	−0.3283	0.7953	−0.9456	0.9086	−0.9402	0.9124
P	NS[a]	<0.001	<0.001	<0.001	<0.001	<0.001

[a] NS, not significant.

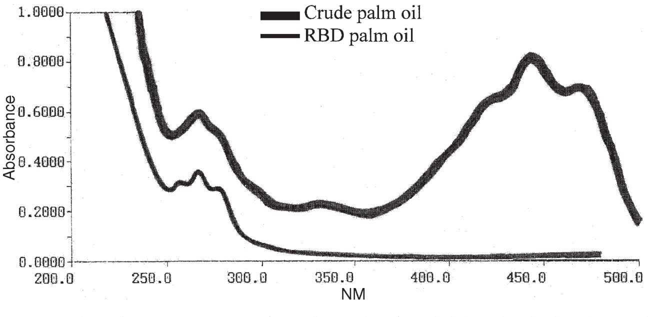

FIG. 1. Absorbance spectra of crude and refined, bleached, deodorized (RBD) palm oil.

TABLE 4
Carotenoid Content and Color Evaluation in Lovibond (Y, R) and CIE (L*, a*, b*) Units in RBD Palm Oil Samples[a]

	Lovibond		CIE			
Palm oil	Y	R	L*	a*	b*	a*/b*
RBD (from C1 + 0.125% S)						
0.5%	21	2.3	97.39	−6.62	32.66	−0.20
0.625%	21	2.2	97.17	−6.33	31.47	−0.20
0.75%	20	2.0	97.48	−6.68	31.07	−0.21
0.875%	20	2.0	98.05	−6.47	30.58	−0.21
1.00%	20	2.0	98.35	−6.17	28.11	−0.22
RBD (from C2 + 0.125% S)						
0.5%	20	2.7	96.90	−6.42	33.60	−0.19
0.625%	21	3.0	97.08	−6.44	33.64	−0.19
0.75%	20	2.5	96.43	−6.29	32.53	−0.19
0.875%	20	2.2	97.63	−6.05	29.59	−0.20
1.00%	20	2.1	97.84	−6.27	29.70	−0.21
RBD (from C3 + 0.125% S)						
0.5%	26	2.5	97.12	−6.58	33.33	−0.20
0.625%	21	2.6	97.03	−6.50	32.33	−0.20
0.75%	27	2.0	97.87	−6.40	30.53	−0.21
0.875%	20	2.2	97.16	−6.45	31.17	−0.21
1.00%	20	2.2	97.74	−6.00	28.91	−0.21

[a] RBD, refined, bleached, deodorized. For other abbreviations, see Tables 1 and 2.

Considering the total amount of identified tocopherols in RBD oil samples (Table 5), it is possible to calculate an average tocopherol retention of 80% compared to crude oil. Lower retention values for tocopherols are generally reported in literature (1,5,13).

The steam-refining treatment causes the removal by stripping of about 200–300 mg/kg of tocopherols, except for the sample treated with 0.625% C1 clay, which shows a 99% tocopherol retention. Owing to problems on the vacuum line, that sample was treated at a higher pressure (7–9 mm Hg) during steam refining, and consequently, it also presented an acidity of 0.08% in the finished oil, compared to an acidity of 0.05% in the other finished samples. The higher operative pressure thus impaired the stripping of both free fatty acids and tocopherols.

The relative concentrations of the single tocopherols were further modified by steam refining, probably owing to differences in volatility among the various forms and, in part, to their different stabilities during the refining process, according to what was reported by Gapor *et al.* (13). The most evident variations in RBD samples were observed for α-tocotrienol, whose relative concentrations were higher compared to both crude and bleached oils, and for δ-tocotrienol, whose relative concentrations were reduced in all cases.

In conclusion, it is possible to affirm that the refining process can be carried out under operative conditions that preserve the majority of palm oil tocopherols. The use of an acid clay and of steam refining under mild vacuum conditions allows a high retention (up to 99%, compared to the crude oil) of these important antioxidants, safeguarding the quality of the finished oil.

This study confirms that the treatment with adsorbent clays and synthetic silica does not affect the color of the finished palm oil, since it depends mainly on the heat bleaching

TABLE 5
Identified Tocopherol Concentrations (mg/kg) in Crude Palm Oil, in Samples Bleached with Different Levels of C1 and 0.125% of S, and in RBD Palm Oil Samples[a]

		Bleached					RBD				
Tocopherols[b]	Crude	0.5%	0.625%	0.75%	0.875%	1.00%	0.5%	0.625%	0.75%	0.875%	1.00%
α-T	190 (25)	220 (28)	247 (31)	233 (29)	276 (31)	223 (27)	147 (27)	200 (26)	125 (25)	176 (26)	150 (25)
α-T3	131 (17)	155 (20)	172 (21)	162 (20)	177 (20)	156 (19)	140 (25)	178 (23)	112 (22)	154 (22)	147 (24)
γ-T3	339 (44)	291 (37)	283 (35)	286 (35)	311 (35)	250 (30)	213 (39)	316 (41)	201 (40)	287 (42)	251 (41)
δ-T3	113 (15)	127 (16)	101 (13)	135 (17)	139 (15)	206 (25)	51 (9)	72 (9)	69 (14)	72 (10)	62 (10)
SUM	773	794	803	815	901	834	551	766	506	688	610

[a] Relative concentrations (g/100 g) are reported in parentheses. For abbreviations, see Tables 1 and 4.
[b] α-T, α-tocopherol; α-T3, α-tocotrienol; γ-T3, γ-tocotrienol; δ-T3, δ-tocotrienol.

process carried out during steam refining, as a consequence of the high temperature applied.

Finally, the tentative application of an objective method for the measurement of palm oil color, based on CIE L*, a*, b* units, demonstrated its excellent repeatability and a significant correlation of the color units with the carotenoid content, as well as its simplicity and rapidity. Therefore, the objective method can be used successfully as an alternative to the classical Lovibond matching method, and for on-line control.

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