The Effect of Carotene Extraction System on Crude Palm Oil Quality, Carotene Composition, and Carotene Stability During Storage

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ABSTRACT: Palm carotene was successfully concentrated from crude palm oil (CPO) by an adsorption process using a synthetic adsorbent followed by solvent extraction. Evaluation of feed CPO and CPO which underwent the carotene extraction process was conducted. The quality of CPO after the extraction process was slightly deteriorated in terms of free fatty acid, moisture content, impurities, peroxide value, anisidine value, discriminant function, and deterioration of bleachability index. However, the CPO still can be refined to produce refined, bleached, deodorized palm oil that meets the Palm Oil Refiners Association of Malaysia specifications. No extra cost was incurred by refining this CPO as the dosage of bleaching earth used was very similar to the refining of standard CPO. The triglyceride carbon number and fatty acid composition of CPO after going through the carotene extraction process were almost the same as CPO data. The major components of the carotene fraction were similar to CPO, which contains mainly α- and β-carotene. The carotene could be stored for at least 3 mon.

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KEY WORDS: Adsorption, palm carotene, palm oil, refining, synthetic adsorbents.

Crude palm oil (CPO) is the world's richest source of natural plant carotenoids in terms of retinol (pro-vitamin A) equivalent (1). It contains about 15 to 300 times more retinol equivalent than carrots, green leafy vegetables, and tomatoes, all of which are considered to have significant pro-vitamin A activity (2). Methods to recover carotenoid from palm oil include saponification (3,4), adsorption (5), selective solvent extraction (6), transesterification followed by distillation, and others (7–10). Only transesterification followed by distillation has been further developed into a commercial-scale process. However, in the latter process, CPO has to be converted to methyl esters, which are not edible.

A process to separate carotene from CPO that did not require converting CPO to methyl esters was successfully developed (11–13); it was based on adsorption with a synthetic polymer adsorbent. The objectives of this study were to evaluate CPO quality after the carotene extraction process, to determine the triglyceride (TG) carbon number and fatty acid composition (FAC) of the CPO, and to determine the carotene composition and its stability during storage.

MATERIALS AND METHODS

Materials. CPO was obtained from Golden Jomalina Food Industries (Teluk Panglima Garang, Selangor, Malaysia). All solvents used were of industrial grade. Synthetic highly porous resin (HP 20) and synthetic porous resin (SP850) (13), both styrene-divinyl benzene copolymers, were obtained from Mitsubishi Chemical Corporation (Tokyo, Japan).

Adsorption. The adsorption process was conducted in a 2000-mL round-bottomed flask. The adsorbent was treated with isopropanol (IPA) for about 15 min with rapid agitation, separated from IPA, and dried at room temperature before use in the adsorption process. The CPO was diluted with three parts of IPA. Diluted CPO was added to the dried adsorbent in the round-bottomed flask at a rate of 10 mL/min. Stirrer speed was maintained at 120 rpm, and temperature at 50–55°C. Adsorption time was *ca.* 30 min.

Solvent extraction. After the adsorption process had been completed, the diluted CPO solution was decanted and adsorbent was transferred to a 2000-mL Soxhlet extractor. The remaining CPO was extracted from the adsorbent with IPA for about 2.5 h at 80–85°C. Carotene was then extracted from the adsorbent at 60–65°C until the adsorbent became colorless (about 4 h). Solvents were removed from the IPA fractions, which contained CPO, and the hexane fractions, which contained carotene, in a vacuum evaporator.

Pilot plant refining. Pilot plant refining of CPO from IPA fractions was conducted to determine whether the CPO from IPA fractions can be refined to meet at least the standard specification of Palm Oil Refiners Association of Malaysia (PORAM) (14).

Degumming. Composite CPO *(*400 mL) from IPA fractions was used. The degumming process was conducted in a 2000-mL round-bottomed flask at 85°C under vacuum (30 mm Hg pressure) with constant stirring. Phosphoric acid (85% concentration) was added to a level of 0.04% (w/w) based on feed oil with stirring for 20 min.

Bleaching. Degummed CPO was bleached at 90°C, under vacuum (30 mm Hg pressure) with constant stirring for 30 min using 1, 2, or 3% (w/w basis) of Wac Supreme (Taiko Clay

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Marketing Sdn. Bhd., Ipoh, Perak, Malaysia) bleaching earth. The oil was then filtered under suction.

Deodorization. Deodorization was conducted by purging the CPO with saturated steam at 260–265°C under 3 mm Hg pressure for about 1.5 h. The quality of the deodorized oil was assessed through the measurement of color, free fatty acid (FFA), moisture, and impurities.

Determination of total carotene. Carotene content was determined by diluting a 1-mL aliquot of each fraction with hexane to the appropriate dilution and measuring absorbance in a Shimadzu UV-1601 (Shimadzu Corporation, Kyoto, Japan) at 446 nm.

High-performance liquid chromatography (HPLC) analysis of carotene. The carotene composition was measured with a Waters 486 HPLC (Millipore Corporation, Milford, MA) equipped with a variable wavelength (190–900 nm) and Crest-Pak $C_{18}S$ MLC-01-250465 (250 × 4.6 mm i.d.) column (JASCO Corporation, Tokyo, Japan). The isocratic mobile phase was acetonitrile/dichloromethane (8:2, vol/vol). The flow rate was 1.0 mL/min, and carotene was determined by measuring absorbance at 446 nm.

TG carbon number composition. TG carbon number composition of feed CPO and CPO from IPA fractions, refined, bleached, deodorized (RBD) palm oil from pilot plant refining, and RBD palm oil from plant production (Golden Jomalina Food Industries) were determined by the Palm Oil Research Institute of Malaysia (PORIM) gas–liquid chromatography (GLC) method (15). Approximately 0.03 g of sample was dissolved in 10.0 mL *n*-hexane, and 1 µL of the sample was injected into the GLC. The injector and detector temperatures were 70 and 350°C, respectively. The first stage flow rate, which was 60 µL/min, was held constant until the temperature reached 290°C. The second-stage flow rate, which was 3 µL/min, was maintained until the temperature reached 350°C. The total cycle time was 23.66 min, and the pressure was 5 kPa. GLC analysis was accomplished with an HP 5890 series II Plus apparatus, equipped with a fused-silica bonded phase column (i.d. 0.53 mm × 6 m length) (Hewlett-Packard, Palo Alto, CA).

FAC. The CPO feed, CPO from IPA fractions, RBD palm oil from pilot plant refining, and RBD palm oil from plant production (Golden Jomalina Food Industries) were analyzed for FAC by converting the TG to fatty acid methyl esters (FAME) with sodium methoxide in methanol and analyzing the FAME by GLC (15).

Analysis of CPO quality. Feed CPO and CPO from IPA fractions were analyzed for FFA, moisture, impurities, peroxide value (PV), anisidine value (AV), iodine value (IV), slip melting point (SMP), ultraviolet measurement at 233 (E_{233}) and at 269 nm (E_{269}), discriminant function (DF), carotene content, deterioration of bleachability index (DOBI), phosphorus, color, and tocopherol content. The analyses were conducted according to the PORIM test methods (14).

RESULTS AND DISCUSSION

TABLE 1
Quality of Feed Crude Palm Oil (CPO) and CPO from Isopropanol (IPA) Fractions

	Samples	
Parameters[a]	Feed CPO[b]	CPO from IPA fractions[b]
FFA (%)	2.50 ± 0.1	2.74 ± 0.1
Moisture (%)	0.031 ± 0.1	0.4 ± 0.3
Impurities (%)	0.014 ± 0	0.033 ± 0
PV (meq/kg)	0.70 ± 0.1	2.03 ± 0.1
AV	0.66 ± 0.2	5.28 ± 0.3
IV	52.88 ± 0.1	52.91 ± 0.1
SMP ((C)	35.8 ± 0.2	36.9 ± 0.5
ABS: 233	1.4110 ± 0.1	1.6568 ± 0.2
ABS: 269	0.5350 ± 0	0.4201 ± 0
DF[c]	22 ± 2.0	2 ± 4.2
Carotene (ppm)	632 ± 15.5	284 ± 18.3
DOBI[d]	3.09 ± 0.1	1.79 ± 0.3
Phosphorus (ppm)	7.05 ± 0	7.04 ± 0
Color, 1″ cell	31R ± 2.0	15R ± 3.7
Tocopherol (ppm)	747 ± 35	725 ± 44

[a] FFA, free fatty acids; PV, peroxide value; AV, anisidine value; SMP, slip melting point; IV, iodine value; ABS, absorbance.
[b] Results have been expressed as mean ± standard error.
[c] Equation 2 (discriminant function).
[d] Equation 1 (deterioration of bleachability index).

Analysis of CPO quality. Table 1 shows the quality of feed CPO and CPO from IPA fractions. Generally, the CPO quality after the carotene extraction process deteriorated slightly in terms of FFA, moisture content, impurities, PV, AV, DF, and DOBI. According to Malaysian Standards (16) for special-quality CPO, FFA should be 2.5% maximum, moisture 0.2% maximum, impurities 0.05% maximum, PV 3 meq/kg maximum, and AV 4 maximum. Specifications for standard-quality CPO are 5% FFA maximum, 0.2% moisture maximum, and 0.05% impurities maximum. For standard quality CPO there are no specifications for PV and AV (15). The FFA of the CPO from IPA fractions increased from 2.5 to 2.74%. This slight increase in FFA may be due to the heating and solvent extraction procedures used during the carotene extraction process. Moisture content of the CPO from IPA fractions increased from 0.031 to 0.40%, and impurities increased from 0.014 to 0.033%. These increases may be due to inefficient solvent (IPA) removal, which contributes to weight loss during determination of moisture content.

Oxidation (primary and secondary) is described in terms of PV and AV. The total oxidation value (TOTOX) is equal to 2PV + AV. Poor-quality oils with high AV are usually organoleptically unacceptable (17). The extent of deterioration of palm oil can be determine by DOBI method (18), which involves spectrophotometric measurements of absorbance at 446 and 269 nm. It is defined in Equation 1:

$$\text{DOBI} = \frac{\text{absorbance at 446 nm}}{\text{absorbance at 269 nm}} \qquad [1]$$

Another useful quality index is DF, which determines the quality in terms of oxidation and bleachability. DF should be incorporated with DOBI into the quality specification. DF involves analysis of PV, carotene content, extinction coefficient at 269 nm, and DOBI. Equations 2 and 3 relate these parameters (17):

TABLE 2
CPO Grade Based on a DOBI and DF Values[a]

DF	DOBI	CPO grade
<0	<1.7	Sludge palm oil or its equivalent quality
1–10	1.8–2.3	Poor
11–20	2.4–2.9	Fair
21–25	3.0–3.2	Good
>25	>3.3	Excellent

[a] Source: Reference 17. See Table 1 for abbreviations.

$$Y_1 = 47.76X_1 + 0.18X_2 + 17.74X_3 - 0.17X_4 - 86.69 \quad [2]$$

$$Y_3 = 47.76X_1 + 0.18X_2 + 1.74X_3 - 0.30X_4 - 59.40 \quad [3]$$

where Y_1 = CPO; Y_3 = sludge palm oil (poor quality palm oil recovered from processing waste that does not meet Malaysian Standard palm oil specifications); $X_1 = E_{269}$ 1%; X_2 = carotene content; X_3 = DOBI; X_4 = PV.

$$Y_1 - Y_3 = \mathrm{DF} = 0.3X_1 + 16X_3 + 0.13X_4 - 27.29 \quad [4]$$

Equations 2–4 can be used to distinguish CPO from sludge palm oil.

Based on the DOBI and DF values, PORIM has proposed CPO quality grades (Table 2). PV and AV of the CPO from IPA fractions were increased from 0.70 to 2.03 and 0.66 to 5.28, respectively. The increases in PV and AV were due to several heating steps and long storage of the CPO. DOBI and DF of the CPO from IPA fractions were decreased from 3.09 to 1.79 and from 22 to 2, respectively, owing to the removal of carotene and to oil oxidation resulting from several heating steps. CPO with DOBI and DF mentioned above were graded as poor-quality oil (17).

Under standard specifications for RBD palm oil, the FFA should be 0.1% maximum, moisture and impurities should be 0.1% maximum, IV should be between 50 and 55, SMP should be between 33 and 39°C, and color (1″ cell) should be 3 red maximum (18). The bleaching earth dosage for normal CPO ranges from 1 to 2% (19). Table 3 shows the quality of CPO from IPA fractions and RBD palm oil using 1, 2, and 3% of bleaching earth, respectively. Based on this pilot plant refining, it was determined that extracted CPO can be refined to produce RBD palm oil that meets PORAM specifications. Because the oil can be bleached with 1% bleaching earth, no extra cost is incurred in comparison with normal CPO.

TG carbon number composition. TG carbon number analyses were performed for the feed CPO, CPO from IPA fractions, RBD palm oil from pilot plant refining, and RBD palm oil from plant production. The TG carbon number composition of CPO from IPA fractions, RBD palm oil from pilot plant refining, and RBD palm oil from plant production were essentially the same as feed CPO (Table 4). That is, the TG carbon number of feed CPO did not change appreciably during the carotene extraction process.

Analysis of FAC. FAC analyses were performed for the feed CPO, CPO from IPA fractions, RBD palm oil from pilot

TABLE 3
Quality of CPO from IPA Fractions and Pilot Plant RBD Palm Oil Using 1, 2, and 3% Bleaching Earth

	1% Bleaching earth		2% Bleaching earth		3% Bleaching earth		PORAM[c] specification
Parameters	CPO[a]	RBD PO[b]	CPO[a]	RBD PO[b]	CPO[a]	RBD PO[b]	for RBD PO[b]
FFA	2.57	0.035	2.83	0.021	2.62	0.011	0.1
M & I[d]	1.312	0.017	0.46	0.008	0.711	0.014	0.1
IV	52.45	52.22	52.88	52.46	53.15	52.80	50–55
SMP (°C)	34.6	35.1	34.7	34.5	35.2	35.5	33–39
Color, 1″ cell	19R 20Y	—	22R 30Y	—	21R 30Y	—	—
Color, $5\frac{1}{4}$″ cell	—	2.8 R 20Y	—	2R 21Y	—	1.3 R 15Y	3 Red Max
DOBI	1.63	—	1.38	—	1.93	—	—

[a] Extracted CPO from IPA fractions.
[b] Refined, bleached, deodorized palm oil.
[c] Palm Oil Refiners Association of Malaysia.
[d] Moisture and impurities. See Table 1 for other abbreviations.

TABLE 4
Triglyceride Carbon Number Composition of Feed CPO, CPO from IPA Fractions, and RBD Palm Oil

	Carbon number (%)					
Samples	C_{46}	C_{48}	C_{50}	C_{52}	C_{54}	C_{56}
Feed CPO	0.5	6.8	38.4	2.4	11.5	0.4
CPO from IPA fraction	0.3	7.1	39.0	41.9	11.1	0.4
RBD palm oil[a]	0.6	7.4	39.4	41.4	10.9	0.4
RBD palm oil[b]	0.5	7.1	39.0	41.9	11.1	0.4

[a] RBD palm oil from plant production (Golden Jomalina Food Industries Sdn. Bhd. Teluk Panglima Garang, Selangor, Malaysia).
[b] RBD palm oil from pilot plant refining. See Tables 1 and 3 for abbreviations.

TABLE 5
Fatty Acid Composition of Feed CPO, CPO from IPA Fractions, and RBD Palm Oil

	Carbon number (%)								
Samples	C_{12}	C_{14}	C_{16}	$C_{16:1}$	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	C_{20}
Feed CPO	0.0	0.6	42.7	0.0	3.9	42.0	0.7	0.0	10.1
CPO from IPA fraction	0.1	0.9	44.0	0.0	3.7	40.8	0.7	0.0	9.7
RBD palm oil[a]	0.0	0.8	43.6	0.0	3.8	41.4	0.7	0.0	9.5
RBD palm oil[b]	0.0	0.7	41.7	0.0	4.0	43.0	0.8	0.0	9.9

[a] RBD palm oil from plant production. See Table 4 for company source.
[b] RBD palm oil from pilot plant refining. See Tables 1 and 3 for abbreviations.

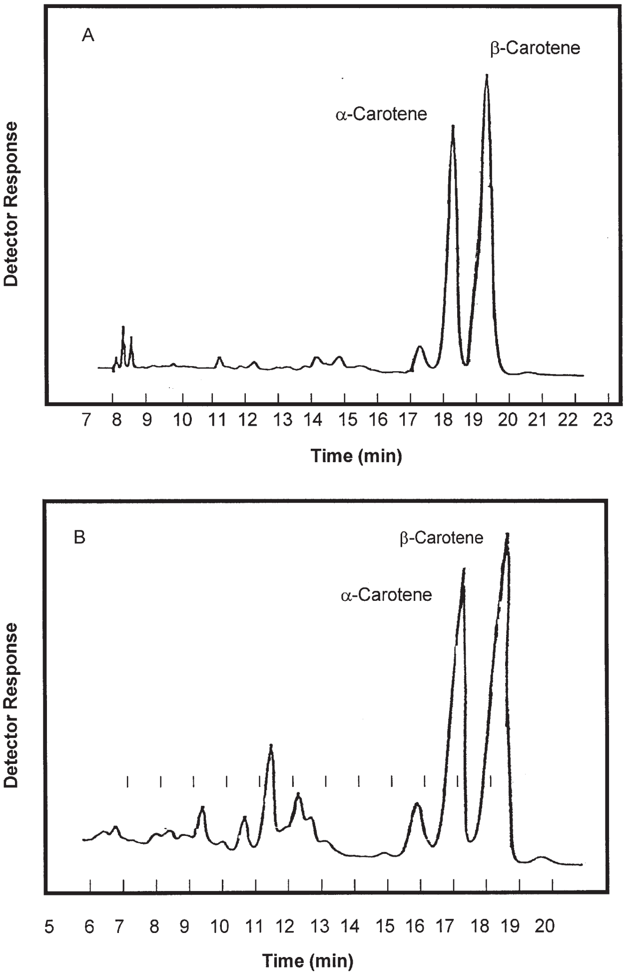

FIG. 1. High-performance liquid chromatograms of carotenes in feed crude palm oil (A) and hexane fraction (B). For conditions, see text.

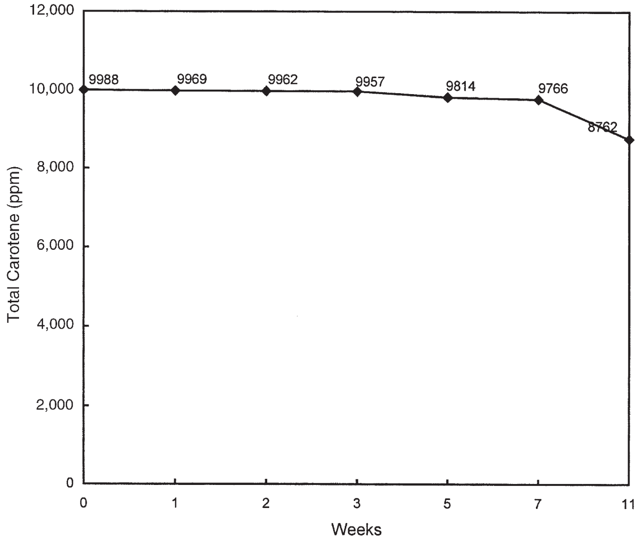

FIG. 2. Carotene stability during storage. The carotene was stored under nitrogen in a glass container covered with aluminum foil in the freezer. Each data point represents three samples. Standard deviations were ± 30 ppm.

plant refining, and RBD palm oil from plant production and were found to be almost the same (Table 5). These results indicate that the FAC of feed CPO does not change appreciably during the carotene extraction process.

Analysis of carotene compositions by HPLC. HPLC analyses of carotene in the hexane fraction showed essentially the same pattern as that in feed CPO (Fig. 1). The major components of carotene in the hexane fraction were similar to feed CPO, which contains mainly α- and β-carotene.

Stability of carotene during storage. The hexane fraction, which contains carotene-rich oil, was stored under nitrogen in a glass container covered with aluminum foil in the freezer. The total carotene content was monitored on a weekly basis, and the results in Figure 2 show that the carotene is stable under these conditions for at least 3 mon.

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