# Effects of Refining on Chemical and Physical Properties of Palm Oil Products

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**Some chemical changes in the composition and physical properties of palm oil products are discussed. The effects of bleaching and deodorization on oxidative properties and possible isomerization and interesterification of the fatty acids were indicated from laboratory refining experiments. Investigation of commercial samples of refined palm oil products showed that the conjugated dienes and trienes formed are minimal, indicating the use of good quality raw materials and mild processing conditions. Very little isomerization occurred in commercial refined products as indicated from the level of *trans* acids, and changes in the POP to PPO triglycerides due to possible interesterification were insignificant. Changes in physical properties were inevitable due to the removal of free fatty acids and diglycerides and to minor impurities.**

Oils are refined to remove undesirable materials such as color bodies, oxidative components, gums, metal contaminants and volatiles. Palm oil is refined by physical processes and involves degumming and bleaching followed by deodorization. During degumming and bleaching, phosphoric acid and activated clay are dosed at temperatures of 90-105°C. Deodorization occurs at 240-280°C for periods ranging from .5 to 2 hr. In physical refining, it is important to ensure that mild conditions are used in order to avoid deleterious effects on oil composition and properties.

The present paper aims at providing some information on the possible changes that may occur to the chemical and physical properties of palm oil under different refining conditions.

## MATERIALS AND METHODS

Crude palm olein, palm mid-fraction, crude palm oils of varying quality, and sets of crude and refined palm oil products were used for the experiments.

*Laboratory refining.* About 500 g of crude palm olein and palm mid-fraction samples were degummed with 0.1% of phosphoric acid at 90° for 10 min. Tonsil Optimum FF bleaching earth (0.5 g) was added, and the oil was stirred vigorously for 15 min at 95°C. The oil was filtered twice through Whatman No. 1 filter paper on a Buchner filter funnel. Deodorization was carried out at different temperatures ranging from 220-280°C for periods ranging from 1 to 4 hr.

Analyses of *trans* fatty acids, fatty acid composition, triglyceride composition and fatty acid at the 2-position of the glyceride were performed on the refined samples. These samples were refined under severe conditions to determine the possible changes that may occur.

Oxidative changes that occur during bleaching and degumming were evaluated on 21 samples of crude and refined palm oil products. Laboratory refining was performed on crude palm oil using different earths at varying dosages. The conjugated dienes and trienes were measured. These were also carried out on various quality crude oils.

*Analysis of fatty acid methyl esters (FAME).* The fatty acid compositions of the oils were analyzed as methyl esters which were prepared by a rapid method; 0.05 g of sample was dissolved in one ml of n-hexane in a screw-capped vial. Then, 0.05 ml of 1 M sodium methoxide was added. The mixture was shaken vigorously for five seconds and then allowed to settle before the hexane layer was pipetted for gas liquid chromatographic (GLC) analysis.

trans *Acids.* FAMEs prepared were analyzed on a 6-m × 3-mm i.d. glass column of 15% OV 275 on a 100-120 mesh Chromosorb P AW-DMCS (Supelco Inc., Bellefonte, Pennsylvania). The column temperature was set isothermally at 220°C and the injector temperature was at 270°C. The carrier gas flow rate (nitrogen) was set at 10 $cm^3$/min. Analyses were carried out on a Perkin Elmer Sigma 2 Gas chromatograph.

A standard palm oil which had been calibrated against a Nu Chek 20 A reference mixture was used for the determination of response factors for the various FAME. *trans* 18:1 FAME was assigned a response factor similar to that for *cis* 18:1 FAME, and *trans, trans* 18:2 and *cis trans* 18:2 were assigned the response factors for *cis, cis* 18:2 methyl esters.

*Triglyceride analysis by carbon number.* A Perkin Elmer Sigma 1 Gas chromatograph was used. Five percent solutions of the samples in chloroform were prepared for analyses. The glass column used was 46 cm × 3 mm i.d. containing 3% OV-1 on 100-120 Gas Chrom Q. The carrier gas was nitrogen at a flow rate of 60-80 ml/min. Detector and injector temperatures of 370°C were used. The column was programmed from 280 to 345°C/min with initial and holding times at the starting and final temperatures set at three min each. Response factors were determined using a standard palm oil reference previously calibrated against a mixture of pure saturated triglycerides.

*Fatty acid at the 2-position.* A semi microlipolysis method was used. Triglycerides were obtained from a column chromatography method (2). The triglycerides (40-60 mg) were melted, dissolved in a few drops of butanol in a test tube (19 × 2 cm) and placed in a water bath maintained at 40°C. Buffer (1.2 M $NH_4CL/NH_4OH$. pH 8.5, 2 ml), calcium chloride solution (22%, 0.2 ml) and bile salts (25%, 0.10 ml) were added. The mixture was stirred slowly by a magnetic stirrer until an emulsion was obtained. Pancreatic lipase (50 mg, previously washed with ether) was then added and the reaction mixture was stirred vigorously for 10 min. The enzymes were inactivated by adding hydrochloric acid (5 M): water (1:1, v/v, 1 ml). The hydrolysate was

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**TABLE 1**

**Effects of Processing on Fatty Acid Composition of Palm Mid Fractions and Palm Olein**

| Sample | Deodorization Temp (°C) | Deodorization Time (hr) | Fatty Acid Composition (%) 14:0 | 16:0 | 18:0 | 18:1t | 18:1c | 18:2ct | 18:2cc | 18:3 | 20:0 | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Crude olein | - | - | 0.9 | 40.2 | 4.2 | - | 41.7 | - | 11.1 | 0.3 | 0.3 | 1.0 |
| Refined olein | 220 | 1 | 0.9 | 40.5 | 4.2 | - | 41.2 | | 11.0 | 0.3 | 0.4 | 1.0 |
| Refined olein | 260 | 2 | 1.0 | 40.5 | 4.3 | - | 41.5 | 0.3 | 10.7 | 0.1 | 0.3 | 1.2 |
| Refined olein | 280 | 4 | 1.0 | 41.1 | 4.4 | 0.4 | 41.0 | 1.7 | 8.4 | 0.2 | 0.4 | 0.8 |
| Crude PMF[a] | - | - | 1.0 | 46.8 | 4.4 | - | 38.2 | - | 8.3 | 0.2 | 0.3 | 0.8 |
| Refined PMF | 220 | 1 | 0.9 | 47.0 | 4.3 | | 38.0 | 0.1 | 8.0 | 0.2 | 0.3 | 0.9 |
| Refined PMF | 260 | 2 | 1.0 | 46.6 | 4.5 | - | 38.5 | - | 8.3 | 0.1 | 0.3 | 0.7 |
| Refined PMF | 280 | 4 | 1.0 | 47.7 | 4.4 | 0.2 | 37.0 | 1.3 | 6.6 | 0.1 | 0.4 | 0.8 |

[a] Palm mid fraction.

**TABLE 2**

**Effects of Processing on Triglyceride Composition of Palm Mid Fraction and Palm Oleins**

| Sample | Deodorization Temp (°C) | Deodorization Time (hr) | Triglyceride Composition (%) C46 | C48 | C50 | C52 | C54 | C56 |
|---|---|---|---|---|---|---|---|---|
| Crude olein | | | 0.2 | 2.2 | 41.8 | 45.2 | 10.2 | 0.2 |
| Refined olein | 220 | 1 | 0.2 | 2.3 | 41.5 | 45.3 | 10.2 | 0.3 |
| Refined olein | 260 | 2 | 0.2 | 2.7 | 41.2 | 44.9 | 10.6 | 0.3 |
| Refined olein | 280 | 4 | 0.5 | 5.5 | 36.4 | 43.9 | 13.2 | 0.2 |
| Crude PMF[a] | - | - | 0.3 | 3.0 | 54.9 | 35.1 | 6.2 | 0.2 |
| Refined PMF | 220 | 1 | 0.4 | 3.1 | 54.2 | 35.1 | 6.7 | 0.2 |
| Refined PMF | 260 | 2 | 0.4 | 3.4 | 53.2 | 35.5 | 7.1 | 0.2 |
| Refined PMF | 280 | 4 | 0.5 | 4.9 | 50.0 | 36.4 | 7.3 | 0.3 |

[a] Palm mid fraction.

extracted with ether ( 2 × 10 ml), washed with water (2 × 10 ml), dried over anhydrous sodium sulphate and concentrated under a stream of nitrogen.

The monoglyceride fraction was separated by preparative TLC (20 × 20 cm$^2$ plates coated with 0.75 mm silica gel). The chromatograms were developed in hexane:ether:formic acid (V/V 50:50:1). The 2-monoglycerides were recovered with ether and transesterified.

*Conjugated dienes and trienes.* These were measured according to PORIM test methods (3) at 233 and 269 nm in a HP 8450A UV-Vis spectophotometer. About 0.12 g of oil in iso-octane in a 25-ml volumetric flask was prepared. The absorbances at 233, 269 and 446 nm were measured against a reference (pure iso-octane) and corrected for cuvette error at these wavelengths. A correction factor was made to account for the carotene absorbance.

*Solid fat content (SFC) measurement by nuclear magnetic resonance (NMR).* A Newport Mark IIIA NMR with temperature controller was used. The instrument was set at gatewidth = 1½ G: R.F. = 45 A, A.F. gain = 375 unit and integration time = 32 sec. Sample weight was ca. 1.5 g, and triolein was used as reference. Parallel tempering procedure was used. A number of tubes of each sample were required but only one tube was held at each of the measuring temperatures. The sample was melted at 70°C for 30 min, chilled at 0°C for 90 min and held at the measuring temperatures for 30 min prior to the reading of signals.

*Cloud point.* Cloud point is the temperature at which a cloud of crystals is induced in the sample caused by the first stage of crystallization. It is defined as the temperature at which the thermometer in the sample no longer appears visible, under the conditions of the test. Cloud points of palm oleins were performed according the AOCS Official Method C.c 6-25 (4).

## RESULTS AND DISCUSSION

*Fatty acid and triglyceride composition.* Table 1 shows the fatty acid composition of palm oleins and palm mid-fractions. Significant changes were observed only when the samples were subjected to 280°C for a four-hour deodorization period. *trans* Fatty acids were absent in the crude and refined samples deodorized at 220 and 260 C for one and two hr respectively. Small amounts of 18:1 *trans* and 18:2 *cis trans* were detectable under conditions of 280°C for four hr. One and one-half and 2.1% of total *trans* acids were observed in the palm olein and palm mid-fractions. The conditions were more extreme than those used in actual commercial processes. Not more than 0.6% of total *trans* acids were reported in commercial refined palm oil products (5). These oils were subjected to deodorization conditions of 260-275°C for 0.75-1.5 hr. Rossell et al. (6) reported up to 10% *trans* acids in soybean oil when refined at 280°C for one hr, while those refined at 240°C for two hr showed a *trans* acid content of 2.3%. Similar findings were reported by Ackman et al. (7) on the detection of artefacts, identified as *cis*-9, *trans*-12, *cis*-15 and *trans*-9, *cis*-12, *cis*-15 isomers of linolenic acid. Some 0.7 to 2.6% of these acids were found in rapeseed vegetable oils from the retail market.

The triglyceride composition in Table 2 shows that intermolecular rearrangement of fatty acid can be observed only in samples subjected to drastic refining conditions. Typically, little or no change is observed in commercially refined oils (8).

**TABLE 3**

**Effects of Refining on the Fatty Acid Composition (%) at the 2-Position of the Glyceride**

| Samples | C14 | C16 | C18 | C18:1 | C18:2 |
|---|---|---|---|---|---|
| Crude palm oil | 0.5 | 14.5 | 1.9 | 63.4 | 19.8 |
| Degummed bleached oil | 0.5 | 15.3 | 1.7 | 62.8 | 19.6 |
| Refined oil | 0.5 | 16.7 | 1.9 | 62.4 | 18.5 |
| Crude palm olein | 0.5 | 8.3 | 1.3 | 68.6 | 21.4 |
| Degummed bleached olein | 0.4 | 8.2 | 1.3 | 68.8 | 21.0 |
| Refined olein | 0.4 | 9.5 | 1.3 | 67.4 | 21.5 |

**TABLE 4**

**Effects of Processing on Physical Properties of Palm Oils and Oleins**

| Sample | Solid fat content | | | | | | | | Cloud point (°C) (mean) |
|---|---|---|---|---|---|---|---|---|---|
| | 5°C | 10°C | 15°C | 20°C | 25°C | 30°C | 35°C | 40°C | |
| Crude palm oil | 60.8 | 49.6 | 34.7 | 22.5 | 13.5 | 9.2 | 6.6 | 4.0 | - |
| Neutralized palm oil | 64.9 | 54.2 | 38.2 | 26.1 | 15.2 | 9.8 | 6.7 | 4.3 | - |
| Refined palm oil | 62.2 | 50.3 | 35.2 | 23.2 | 13.7 | 8.5 | 5.8 | 3.5 | - |
| Crude palm olein | 49.6 | 33.6 | 12.6 | 3.2 | - | | | | 10.4 |
| Neutralized palm olein | 55.4 | 40.3 | 20.4 | 5.3 | - | | | | 8.1 |
| Refined palm olein | 51.1 | 37.0 | 19.2 | 5.9 | - | | | | 8.8 |

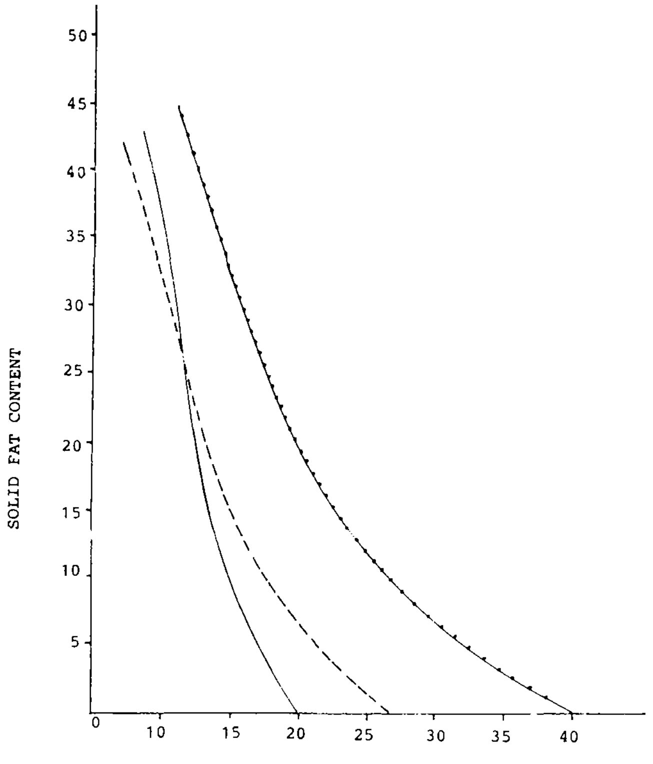

**FIG. 1. Effect of processing on solid fat content of palm oleins, ————, crude palm olein, ---------, refined olein, deodorization 250°C, 2 hr; .........., refined olein, deodorization 280°C, 4 hr.**

Interesterification may occur during deodorization, resulting in an increase in the saturated fatty acids at the 2-position of the glyceride (Table 3). Although there appears to be a slight increase in the palmitic acid content of 1-2%, the increase may not be considered significant as crude palm oil has a palmitic acid content at the 2-position of 14.4 to 18.1% (range of 7 samples studied).

The effect of time and temperature on the POP:PPO ratio of palm oil was discussed by Williams (9). The change in the ratio was significant if the oil was subjected to temperatures of above 270°C for long residence times. Special care taken during the refining process can minimize the change in the symmetrical triglyceride content (POP) to the unsymmetrical triglyceride (PPO).

*Physical properties of palm oil.* In removing impurities, i.e., free fatty acids and diglycerides, refining results in changes in the physical properties of the oil. These differences are observed in the oils (Table 4). Tan et al. (8) reported increased values in solid fat content in refined palm oils compared to crude oils at the lower temperature range (5-20°C).

The overall increase in solid fat content in refined oils is dependent on deodorization conditions. Figure 1 shows the effect of refining conditions on solid fat content of palm olein. The tailing observed in palm olein subjected to 280°C for four hr is highly significant and would affect the oil's crystallization behavior. Although cloud points of palm oleins are generally reduced during refining, the tailing effect produced by interesterification of the fatty

**TABLE 5**

**Conjugated Dienes and Trienes of Bleached Oils (150°C for .5 hr)**

| | Dosage of bleaching earths (%) | | | | |
|---|---|---|---|---|---|
| | 0 | 0.5 | 1.0 | 1.5 | 2.0 |
| $E^{1\%}_{233}$ | 1.76 | 1.52 | 1.67 | 1.90 | 2.42 |
| $E^{1\%}_{269}$ | 0.22 | 0.77 | 0.73 | 0.70 | 0.60 |

**TABLE 6**

**Effect of Refining on Conjugated Dienes and Trienes of Various Quality Crude Oils**

| | $E^{1\%}_{233}$ | | | $E^{1\%}_{269}$ | | |
|---|---|---|---|---|---|---|
| Samples | Crude | Bleached | Refined | Crude | Bleached | Refined |
| Good | 1.05 | 0.90 | 1.46 | 0.19 | 0.29 | 0.19 |
| Average | 1.76 | 1.30 | 1.60 | 0.21 | 0.90 | 0.81 |
| Oxidized | 4.88 | 2.41 | 2.79 | 0.70 | 2.85 | 2.51 |

**TABLE 7**

**Conjugated Dienes in Commercial Refined Palm Oil Products**

| Sample | Mean[a] | Min | Max |
|---|---|---|---|
| Crude palm oil | 1.8 | 1.2 | 2.7 |
| Degummed bleached palm oil | 1.4 | 1.1 | 1.7 |
| Refined palm oil | 1.9 | 1.5 | 2.2 |
| Crude palm olein | 2.1 | 1.5 | 2.9 |
| Degummed bleached olein | 1.5 | 1.2 | 1.9 |
| Refined palm olein | 2.0 | 1.2 | 2.6 |
| Crude palm stearin | 1.7 | 1.4 | 2.4 |
| Degummed bleached stearin | 1.5 | 1.2 | 1.7 |
| Refined palm stearin | 1.6 | 1.0 | 2.0 |

[a]Based on a total of 21 samples.

**TABLE 8**

**Conjugated Trienes in Commercial Refined Palm Oil Products**

| Sample | Mean[a] | Min | Max |
|---|---|---|---|
| Crude palm oil | 0.3 | 0.2 | 0.6 |
| Degummed bleached palm oil | 0.7 | 0.3 | 1.0 |
| Refined palm oil | 0.5 | 0.3 | 0.8 |
| Crude palm olein | 0.3 | 0.2 | 0.4 |
| Degummed bleached olein | 0.9 | 0.5 | 1.5 |
| Refined palm olein | 0.7 | 0.4 | 1.0 |
| Crude palm stearin | 0.4 | 0.2 | 0.7 |
| Degummed bleached stearin | 0.7 | 0.5 | 1.0 |
| Refined palm stearin | 0.5 | 0.3 | 0.7 |

[a]Based on a total of 21 samples.

acids at high temperatures would result in early crystallization of palm olein on storage.

*Oxidative changes.* During bleaching of vegetable oils, color pigments and other impurities are adsorbed. In oils containing PUFAs, conjugated dienes, trienes and tetraenes are formed.

The formation of the conjugated dienes and trienes in palm oil is shown in Tables 5 and 6. The amount of conjugated dienes measurable at 233 nm depended on the dosage of bleaching earths used, more being formed with higher earth dosage. A reduction was observed when low earth dosage of 1% and below was used. This was due to conjugated hydroperoxides being broken down during bleaching. Dehydration of hydroxy compounds may occur (11) especially with high earth dosages and longer bleaching time resulting in higher amounts of dienes formed.

An increase in conjugated trienes was observed during bleaching, which depended on the quality of the crude oil. The effect of earth dosage was minimal. The amount of trienes in oils refined from oxidized crude material was 13 times that formed in oils refined from good quality crude oils. Some of the conjugated trienes are removed later, during deodorization.

The formation of conjugated dienes and trienes in commercial refined palm oil products is minimal (Tables 7 and 8), indicating the use of good quality crude oils as raw feedstock and mild processing conditions.

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