# REFINING OF RED PALM OIL

**Keywords**: Palm oil; carotenes; vitamin E; molecular distillation and deodorization

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process has been developed for the refining of crude palm oil (CPO) to produce Red Palm Oil (RPO) without destroying the carotenes. It involves a pretreatment of CPO followed by deacidification and deodorization using molecular distillation. The RPO produced has less than 0.1% of free fatty acid (FFA) and retains more than 80% of the original carotenes and vitamin E originally present in the CPO. The quality of RPO is similar to that of any refined, bleached and deodorized palm oil in terms of FFA and peroxide value (PV). The carotene profile of RPO showed that most of the carotenes were retained. The process has been commercialized and the product is expected to be in the market soon.

# INTRODUCTION

n he orange-red colour of crude palm oil . (CPO) is due to the presence of carotenes of which the concentration in CPO ranges from 500 to 700 ppm. Apart from carotenes, CPO contains other minor components such as sterols. tocopherols and tocotrienols. phospholipids, squalene, and triterpenic and aliphatic hydrocarbons (Table 1) (Maclellan, 1983; Rossell et al., 1983; Goh et al., 1982; Jacobsberg, 1974; Itoh et al., 1973a, 1973b). Among these minor components, the carotenoids, tocopherols and tocotrienols are the most important. Together they contribute to the stability and nutritional properties of palm oil.

There are 13 different carotenes in CPO. The major components are  $\alpha$ - and  $\beta$ -carotene (Table 2) (Yap et al., 1991), which together constitute more than 90% of the total carotenes. The

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TABLE 1. MINOR COMPONENTS IN PALM OIL

| Components                 | Content (ppm) |
|----------------------------|---------------|
| Carotenoids                | 500-700       |
| Tocopherols and tocotriend | ols 600-1000  |
| Sterols                    | 326-527       |
| Phospholipids              | 5-130a        |
| Triterpene alcohol         | 40-80         |
| Methyl sterols             | 40-80         |
| Squalene                   | 200-500       |
| Aliphatic alcohol          | 100-200       |
| Aliphatic hydrocarbons     | 50            |

<sup>&</sup>lt;sup>a</sup>Goh et al. (1985)

TABLE 2. CAROTENOIDS COMPOSITION OF CRUDE PALM OIL AND RPO

|                | CPO  | RPO   |
|----------------|------|-------|
| Phytoene       | 1.3  | 2.0   |
| Phytofluene    | 0.1  | 1.2   |
| Cis-β-Carotene | 0.7  | 0.8   |
| β- Carotene    | 56.0 | 47.4  |
| α- Carotene    | 35.1 | 37.0  |
| Cis-α-Carotene | 2.5  | 6.9   |
| ζ- Carotene    | 0.7  | 1.3   |
| δ- Carotene    | 0.3  | 0.5   |
| γ- Carotene    | 0.8  | 0.6   |
| Neurosporene   | 0.3  | trace |
| β- Zeacarotene | 0.7  | 0.5   |
| α- Zeacarotene | 0.2  | 0.3   |
| Lycopene       | 1.3  | 1.5   |
| Total (ppm)    | 673  | 545   |

<sup>\*</sup>Choo et al. (1992)

tocopherols and tocotrienols found in CPO are αand  $\gamma$  - tocopherols, and  $\alpha$ ,  $\gamma$  -and  $\delta$ -tocotrienols (Table 3) (Gapor et al., 1983). The carotenoids, tocopherols and tocotrienols are effective natural antioxidants. The carotenoids, particularly \betacarotene, are also precursors of vitamin A and studies have shown that various carotenoids possess protective properties against certain types of cancers (Alam et al., 1984; Mathews-Roth et al., 1982; Peto et al., 1981; Suda et al., 1986; Swartz et al., 1986; Staehelin et al., 1984). The tocopherols and tocotrienols function as vitamin E and they have important physiological properties. Studies have shown that they can lower the blood cholesterol level and also prevent aggregation of platelets in blood (Kato et al., 1985; Qureshi et al., 1991; Tan and Chu, 1991).

Most of the palm oil products sold in the market are in the refined, bleached and deodorized (RBD) form. Refining is necessary to remove impurities and contaminants which affect the quality of the end products. However it is important that the refining process retains as much as possible of the natural antioxidants (tocopherols and tocotrienols) to maintain the stability of the oil. Most CPO is refined through the physical process although a small percentage is refined through the chemical process. In the physical refining process, CPO is degummed

TABLE 3. TOCOPHEROLS AND TOCOTRIENOLS IN CRUDE PALM OIL (PPM)\*

| Composition   | (PPM) |
|---------------|-------|
| α-Tocopherol  | 279   |
| γ-Tocopherol  | 61    |
| α-Tocotrienol | 274   |
| γ-Tocotrienol | 398   |
| δ-Tocotrienol | 69    |
| Total         | 1081  |

<sup>\*</sup>Gapor et. al. (1983)

<sup>&</sup>lt;sup>a</sup>Expressed as phosphorus

with about 0.1% phosphoric acid, followed by treatment with about 1% of bleaching earth. The pretreated CPO is then subjected to steam refining under a 3-5 torr vacuum at 250°C-270°C. During the degumming and bleaching stages, the gums, trace metals, oxidation products and some carotenes are reduced or removed. The free fatty acids (FFA), some tocopherols and tocotrienols, monoglycerides, oxidation and pigment decomposition products are removed during the deodorization stage and condensed as palm fatty acid distillates. With the chemical refining process, the CPO is degummed, followed by neutralization with an alkali. The neutralized and degummed palm oil is then treated bleaching earth and deodorized. The high temperature and vacuum used in the deodorization stage is necessary in order to remove as much of the oxidation products as possible. Their presence in the oil would impart a poorer taste to the end product and reduce oxidative stability. Under these conditions some of the tocopherols and tocotrienols are removed and all the carotenes are destroyed. Hence the RBD palm oil from these two refining processes contains about 300–500 ppm of tocopherols

and tocotrienol and no carotene (Table 4) (PORAM, 1993).

This paper describes a new process developed in PORIM (Ooi *et al.*, 1993) which is able to produce a refined palm oil that retains its natural carotenes and vitamin E.

# **EXPERIMENTAL**

### **Materials**

The CPO used in this study was obtained from several local palm oil mills. Commercial bleaching earths were used. All solvents used were of analytical grades.

# **Analysis**

The various quality parameters such as FFA, peroxide value, vitamin E, iron and phosphorus of CPO and RPO were determined through either AOCS (1974) or IUPAC methods (1979).

The carotene profile of RPO was carried out using reverse phase HPLC columns (Zorbox ODS) and a solvent mixture of acetonitrile (89%) and methylene chloride (11%) as described in Yap *et al.* (1991).

TABLE 4. PARAMETERS OF REFINED, BLEACHED AND DEODORIZED (RBD)
PALM OIL AND PALM OLEIN

| Parameter                  | Content      |                |  |
|----------------------------|--------------|----------------|--|
|                            | RBD Palm Oil | RBD Palm Olein |  |
| Free fatty acid (%)        | 0.1 max      | 0.1 max        |  |
| Peroxide value(meq/kg)     | 5.0 max      | 5.0 max        |  |
| Moisture and impurities(%) | 0.1 max      | 0.1 max        |  |
| Colour (5 1/4" Lovibond)   | 3 Red(max)   | 3 Red(max)     |  |
| Melting point (°C)         | 33-39        | 24 max         |  |
| Iodine value (Wij's)       | 50-55        | 56 max         |  |
| Carotenes                  | Nil          | Nil            |  |

\*PORAM (1981)

#### Methods

The refining process consists of a pretreatment stage which involves degumming and bleaching. After this pretreatment a second stage (deacidification and deodorization) completes the process.

The general method of the refining process carried out are described below. CPO was degummed with phosphoric acid (0.5%) at  $90^{\circ}$ C for 10 minutes, followed by bleaching earth (0.2 to 2%) at  $105^{\circ}$ C- $110^{\circ}$ C for 15-30 minutes. The oil was filtered to remove the bleaching earth. The pretreated oil was then heated to  $130^{\circ}$ C- $200^{\circ}$ C and passed through a short path distillation unit at a rate of 24 g per hour and under vacuum  $(20-60 \times 10^{-3} \text{ torr})$ .

The pretreatment stage (degumming and bleaching) was carried out with different percentages of various bleaching earths. The deacidification and deodorization were carried out using various temperatures and vacuum conditions.

The optimum conditions determined in this way are described below. The degumming and bleaching were carried out using phosphoric acid (0.5%) at 90°C for 10 minutes, followed by bleaching earth (0.2%) at 110°C for 30 minutes. The deacidification and dedorization were carried out at 150°C–170°C and vacuum of 20–25  $\times$  10<sup>-3</sup> torr.

# **RESULTS AND DISCUSSION**

he technology for refining red palm oil stage is the pretreatment, which includes degumming of the oil with phosphoric acid, followed by treatment with bleaching earth. The objective of this pretreatment is to remove impurities and oxidation products in crude palm oil without removing or destroying the carotenes. The second stage of the process is deacidification and deodorization. Here, the pretreated oil is passed through a short-path distillation unit at a certain temperature and vacuum. This removes the free fatty acids and odour without destroying In the conventional refining the carotenes. process, most of the carotenes are destroyed during the deacidification and deodorization stages, as already noted.

The second step of the pretreatment process was carried out with eleven different types of bleaching earth and also with trisyl silica (a bleaching aid). In the presence of trisyl silica, the peroxide value was reduced in all the samples, and some reduction (9% to 23%) of the carotene content of almost all the samples were observed (Table 5). In the absence of trisyl silica, five bleaching earths (0.5 w/w %) namely, Pureflo (activated), Tonsil Std. FF, Pureflo M65, Pureflo M80 and Pureflo M85 were not effective in reducing the peroxide value (Figure 1). These bleaching earths also reduced the carotenes by 40% to 53% (Figure 2). Increasing the percentage of bleaching earth and time of bleaching improved removal of peroxides but reduced the carotene content of the oil by more than 50% (Figures 1 and 2).

The other six bleaching earths, Sienna, Tonsil Optimum FF, WAC 100, WAC 100 E, WAC Supreme and Fulmont AA were more effective in reducing the peroxide value in the absence of trisyl silica (Figure 3). There was a smaller loss of carotene (14% to 37%) as compared to the previous group of bleaching earths (Figures 2 and 4). Similarly, increasing the percentage of bleaching earth improved the removal of peroxides but also increased the removal of carotenes from the oil samples (Figures 3 and 4). With 2% of bleaching earth, 31% to 78% of the carotenes were removed (Figure 4).

Among this second group of bleaching earths, WAC 100 is widely used by the palm oil refining industry. Experiments conducted using WAC 100 showed that it could remove the peroxides effectively without reducing the carotene content of the oil (Figures 3 and 4). Increasing the percentage of WAC 100 and the time of bleaching did not improve the removal of peroxides but reduced the carotene content by 6% to 33% (Figures 5 and 6). Varying the temperature from 90°C to 130°C during bleaching did not improve the removal of peroxides but a slight reduction in the carotene content of the oil (8% to 11%) was observed (Figure 7). The results showed that the most suitable pretreatment condition is with 0.2% bleaching earth WAC 100 for 30 minutes at 110°C.

TABLE 5. DIFFERENT BLEACHING EARTH IN THE PRETREATMENT OF CRUDE PALM OIL

| Bleaching Earth     | Free Fatty<br>Acid<br>% | Peroxide<br>Value<br>meq/kg | Carotenes<br>(ppm) |
|---------------------|-------------------------|-----------------------------|--------------------|
| Control             | 2.20                    | 1.00                        | 648                |
| Pureflo (Activated) | 2.30                    | 0.23                        | 570                |
| Tonsil Std. FF      | 2.30                    | 0.20                        | 590                |
| Pureflo M65         | 2.25                    | 0.20                        | 555                |
| Pureflo M85         | 2.20                    | 0.20                        | 573                |
| Pureflo M80         | 2.20                    | 0.20                        | 516                |
| Sienna              | 2.20                    | 0.20                        | $\boldsymbol{442}$ |
| WAC Supreme         | 2.20                    | 0.15                        | 364                |
| WAC 100             | 2.20                    | 0.20                        | 528                |
| WAC 100E            | $\sim 2.20$             | 0.15                        | 531                |
| Fulmont AA          | 2.20                    | 0.15                        | 560                |
| Tonsil Optimum FF   | 2.20                    | 0.10                        | 493                |

 $^{\circ}$ CPO was treatment with 0.5% phosphoric acid for 10 min at 90°C; this was followed by treatment with 0.5% of a bleaching earth with 0.2% of Trisyl silica for 30 min at 110°C.

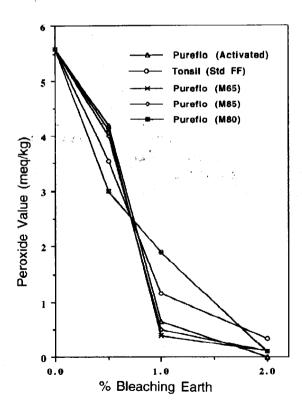


Figure 1. Peroxide values of crude palm oil after pretreatment with different bleaching earths at 105°C for 15 minutes.

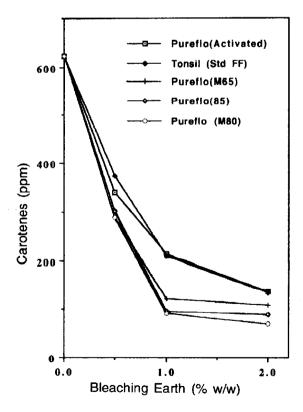


Figure 2. Carotene content of crude palm oil after pretreatment with different bleaching earths at 105°C for 15 minutes.

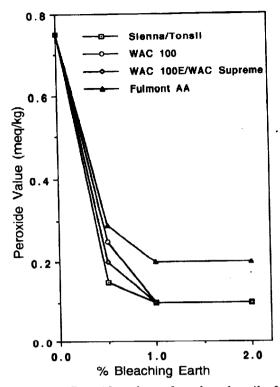


Figure 3. Peroxide values of crude palm oil after pretreatment with different bleaching earths at 110°C for 30 minutes.

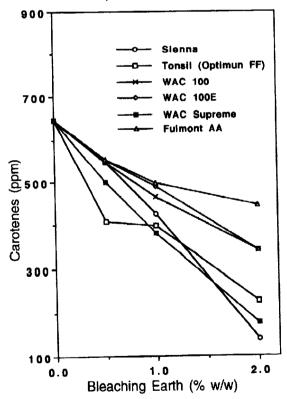


Figure 4. Carotene content of crude palm oil after pretreatment with different bleaching earths at 110°C for 30 minutes.

The deacidification and deodorization of the pretreated palm oil were conducted at  $130^{\circ}\text{C} - 200^{\circ}\text{C}$  at a vacuum of  $20-60 \times 10^{-3}$ Torr. The results showed that this process was able to reduce the free fatty acids (FFA) to 0.02% without reducing or destroying the carotene content (Figures 8 and 9). For a CPO sample with carotene content of 662 ppm and FFA of 2.40%, the RPO had a carotene content of 622 ppm and FFA of 0.03 percent. At a vacuum between  $20 \times 10^{-3}$  Torr and  $60 \times 10^{-3}$ Torr and a temperature between 130°C and 170°C, the RPO retained at least 80% of the carotenes (Figure 8). However at a higher temperatures, 200°C the carotenes were reduced by more than 50 percent. The results showed that increasing the temperature and vacuum removed the FFA more effectively but the high temperature destroyed the carotenes, particularly at temperatures above 170°C.

The RPO retains its tocopherols and tocotrienols as well as from the carotenes (*Table 6*). However, the tocopherols and tocotrienols

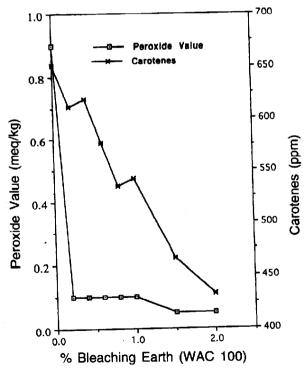


Figure 5. Peroxide value and carotene content of crude palm oil after treating with 0.5% phosphoric acid for 10 min at 90°C and then with different percentages of WAC 100 at 110°C for 30 minutes.

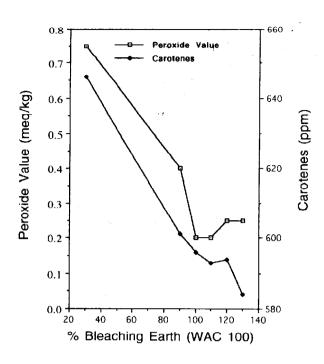


Figure 6. Peroxide value and carotene content of crude palm oil after treating with 0.5% phosphoric acid for 10 min. at 90°C and then with 0.2% WAC 100 for 30 minutes at different temperatures.

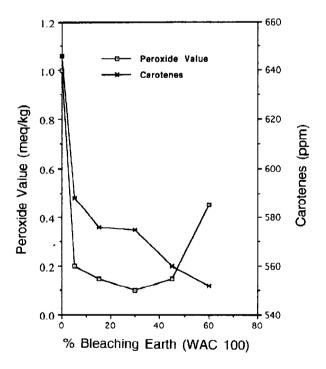


Figure 7. Peroxide value and carotene content of crude palm oil after treating with 0.5% phosphoric acid for 10 min. at 90°C and then with different percentages of WAC 100 at 110°C for different times.

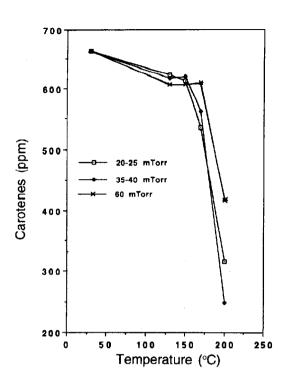


Figure 8. Carotene content of crude palm oil after pretreatment followed by deodorization and deacidification at various temperatures and vacuum.

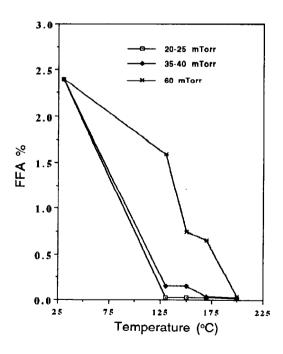


Figure 9. Free fatty acid content of palm oil after pretreatment followed by deodorization and deacidification at various temperatures and vacuum.

were very much reduced when the palm oil was processed at a higher temperature (above  $170^{\circ}$ C). At a temperature of  $130^{\circ}$ C and a vacuum of  $20-60\times10^{3}$  Torr the RPO retained more than 78% of the tocopherols and tocotrienols. However, at temperatures higher than  $170^{\circ}$ C and a vacuum of  $20-25\times10^{-3}$  Torr, more than 77% of the tocopherols and tocotrienols were removed. The phosphorus and iron content of the RPO were also reduced to 0.3 ppm and 2.0 ppm respectively (*Table 6*).

The results of these experiments showed that suitable conditions for refining palm oil without destroying the carotenes are  $150^{\circ}\text{C}$ – $170^{\circ}\text{C}$  and a vacuum of  $20-25 \times 10^{-3}$  Torr.

The process of producing RPO has been successfully scaled up from the laboratory to a pilot plant using the optimum refining conditions. The process technology has been transferred to the industry and commercial production of the red palm oil is expected to begin in 1996.

TABLE 6. PROPERTIES OF CRUDE PALM OIL AND RED PALM OIL

|                        | Crude<br>Palm Oil | Red<br>Palm Oil |
|------------------------|-------------------|-----------------|
| Free Fatty Acid %      | 2.40              | 0.04            |
| Peroxide Value (meq/kg | 0.80              | 0.20            |
| Carotenes (ppm)        | 660               | 531             |
| Vitamin E (ppm)        | 923               | 642             |
| Iron (ppm)             | 3.3               | 0.3             |
| Phosphorus (ppm)       | 7.8               | 2.7             |

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