Palm Oil

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ABSTRACT

Since its arrival in Malaysia as an ornamental plant in 1897, the oil palm *Eleais guineensis* has achieved a position of economic significance to Malaysia. With a current annual production of 2,8 million tons, palm oil has ceased to be traded as a true primary commodity since it is predominantly traded in semi- and fully processed forms. Although palm oil may be handled by classical refining techniques, steam-refining is gaining in popularity for economic and environmental reasons. With the application of physical refining techniques, due attention must be paid to the consequences of mishandling the minor constituents present in palm oil if consistent product integrity is to be achieved and maintained.

INTRODUCTION

As a consequence of the establishment of the oil palm *Elaeis* guineensis as a plantation crop, Malaysia's crude palm oil production in 1981 was 2.82 million tons. Plantation cultivation ensures that there is virtually guaranteed production with any major fluctuation being climatic. With a population in the region of 15 million, Malaysia's relatively small domestic market requires her to develop fully the export potential of this commodity.

This development is being vigorously pursued with the establishment of 48 refinery complexes in West Malaysia and 1 in East Malaysia. These complexes vary widely in throughput and degree of sophistication. Plant capacities range from 30 MT/24 hr to 700 MT/24 hr, the average being in the region of 300-400 ton/24 hr. Most of the installations incorporate fractionation facilities installed as the second stage of the export development program. The next logical step, already underway, is the diversification into palm oil derived fatty acid production, soon to be followed by the production of fatty alcohols and amines. With the exception of perhaps three or four installations, the industry is wholly export-oriented.

Palm oil is a fruit flesh fat derived from the species *Elaeis* guineensis and in some respects may be considered to have more in common with olive oil than with the range of solvent extracted seed oils.

The palms in Malaysia are derived from only four imported seeds, so it is not surprising that their fatty acid compositions fall into a relatively narrow range, much narrower than that allowed by the Codex Alimentarius.

The fatty acid composition of palm oil has been the subject of several surveys by the Malaysian Agricultural Research and Development Institute (MARDI) and the Palm Oil Research Institute of Malaysia (PORIM). Table I shows the results obtained by PORIM.

The glyceride composition of Malaysian palm oil in terms of carbon number is shown in Table II with further analytical characteristics given in Table III.

Reference to these three tables suggests that palm oil, definable in terms of standard parameters, is just another vegetable oil which will behave and be handled as such. It is becoming increasingly apparent however, that this is not so and there are significant deviations from other fats and oils.

The crude palm oil under discussion is already a highly purified entity which has been given a water wash in the course of production which results in incidental degumming. Indeed, the normal levels of moisture and dirt are less than



the experimental error allowed in the BSI/ISO official analytical methods.

TABLE I

Fatty Acid Composition of Palm Oil (1)

| Fatty acid | PORIM | 4 | CODEX |
|-----------------|-----------|------|-----------|
| composition (%) | Range | Mean | Range |
| 12:0 | 0.1-1.0 | 0.2 | 1.2 |
| 14:0 | 0.9-1.5 | 1.1 | 0.5-5.9 |
| 16:0 | 41.8-46.8 | 44.0 | 32.0-59.0 |
| 16:1 | 0.1-0.3 | 0.1 | 0.6 |
| 18:0 | 4.2-5.1 | 4,5 | 1.5-8.0 |
| 18:1 | 37.3-40.8 | 39.2 | 2.7-52.0 |
| 18:2 | 9.1-11.0 | 10.1 | 5.0-14.0 |
| 18:3 | 0-0.6 | 0.4 | 1.5 |
| 20:0 | 0.2-0.7 | 0.4 | 1.0 |

TABLE II

Malaysian Palm Oil - Composition by Carbon Number (2)

| Carbon number | Range | Mean |
|---------------|-----------|------|
| C 46 | 0.4- 1.2 | 0.8 |
| C 48 | 4,7-10.8 | 7.4 |
| C 50 | 40.0-45.2 | 42.6 |
| C 52 | 38.2-43.8 | 40.5 |
| C 54 | 6.4-11.4 | 8.8 |

TABLE III

Additional Analytical Characteristics of Malaysial Palm Oil (3)

| Parameters | Range | Mean | |
|--------------------------------------|---------------|--------|--|
| Relative density @ 50 C/water @ 25 C | 0.8919-0.8932 | 0.8927 | |
| Refractive index Nහ | 1.4546-1.4560 | 1.4553 | |
| Saponification value MgKOH/g oil | 190,1-201.7 | 195.7 | |
| Unsaponifiable content (%) | 0.15-0.99 | 0.51 | |

The soluble impurities in crude palm oil are defined as gums or sludge consisting essentially of phospholipids and metal complexes, peroxides and their breakdown products, pigments, free fatty acids and diglycerides.

The deviations of most significance to the processor are phospholipid content, carotenoid content, free fatty acid content, and iron/tocopherol content. The diglyceride content (4-5%) has important implications for the end user.

Excepting the free fatty acid (FFA) content, the other components are usually termed "minor constituents." While minor in quantity, their effect on final product quality through insufficient or improper handling can be major.

PHOSPHOLIPIDS

The phospholipid content of crude palm oil essentially varies with the season and to a lesser extent with mill operation. The phosphorus content can range from much less than 10 ppm for high quality crude to in excess of 35 ppm. There is some innate deterioration in the fruit after harvesting which gives rise to increased gum and FFA levels. These rises can be partially contained by rapid fruit sterilization at the mill.

The phospholipids and their associated metal complexes are nonhydratable or not easily hydratable, with changes in their character which appear to occur as a result of oil abuse. The metal complexes require acid treatment or conditioning to facilitate their reduction or removal at the "gum conditioning" step.

The usual treatment at the conditioning stage in Malaysia is to contact the oil under controlled time and temperate conditions with 0.1% phosphoric acid. In alkali plants, unreacted phosphoric acid is neutralized with aqueous caustic soda and then precipitated free fatty acids and conditioned gums are removed by centrifuging.

Since no alkali is used in steam or physical refining plants, great reliance is placed on the bleaching earth, at the next process stage, to absorb unreacted phosphoric acid, conditioned phospholipids and metal complexes. Always present is the possibility of phosphoric acid "slip" or carry through, leading to deodorizer pitting inter alia.

In an effort to prevent this slip, the use of calcium carbonate, in the role of chemical trap filter, in conjunction with bleaching earth, has been advocated. Some authors advise application before the bleaching earth addition, while others advise it should be added after the earth. PORIM can find no reason, in terms of quality improvement, to add calcium carbonate either before or after the addition of bleaching earth.

This is only part of a PORIM investigation into the pretreatment stage in palm oil refining. With the tremendous increase in the use of physical refining plants, the pretreatment stage is even more critical than in the past and we believe that it requires a more thorough investigation than it has so far received. Residual phosphorus in a refined, bleached and deodorized (RBD) oil – by virtue of poor treatment – correlates well with free fatty acid escalation during transport. The analyses in Figure 1 are of out-turn oil after a 6-8-week voyage.



FIG. 1. FFA/phosphorus correlation.

In crude palm oil, the complexed metal (usually referred to as iron content) is almost completely derived from wear in rotating machinery in the oil mill. As produced, an average crude palm oil in Malaysia will have around 5 ppm, although significant reduction is possible. The low iron contents for mill D in Table IV are due to the use of stainless steel at specific areas in the process.

TABLE IV

Crude Palm Oil ~ Iron Contents (ppm) during Process

| | Palm oil | | | | | | |
|------------------------|----------|-----|-----|-----|--|--|--|
| Stage of process | A | В | С | D | | | |
| After vibrating screen | | | 3.6 | | | | |
| Before clarifier | | 3.5 | 3.1 | | | | |
| After clarifier | 3.0 | 4.1 | 4.7 | 0.9 | | | |
| After purifier | 2.9 | 4.3 | 6.1 | 0.6 | | | |
| After drier | 3.2 | 4.9 | 5.6 | 0.9 | | | |
| Storage tank | 4.8 | | | 1.2 | | | |

These levels are reduced to 0.05% or less during processing. The crude palm oil under discussion should not be compared too closely with the crude palm oil which, until relatively recently, was the subject of international trade. The average age of crude palm oil on refining in Malaysia is about one month. The iron content is partly particulate and may be much reduced by filtration or even by the use of magnetic pipeline inserts, as shown in Table V.

TABLE V

Iron Content of Crude Palm Oil (4)

| | Iron content (ppm) | | | | | |
|--------------|--------------------|-------------|-------|-------------|--|--|
| | Be | fore traps | A | fter traps | | |
| | Total | Particulate | Total | Particulate | | |
| 8/5 | 4.0 | 1.3 | 3.6 | 1.2 | | |
| 9/5 | 5.0 | 2.9 | 3.8 | 1.8 | | |
| 10/5 | 5.3 | 2.2 | 4.6 | 1.5 | | |
| 12/5 | 9.5 | 6.0 | 5.4 | 1.9 | | |
| 13/5 | 6.0 | 2.3 | 4.0 | 1.0 | | |
| 14/5 | 3.5 | 0.6 | 3.2 | 0.4 | | |
| Overall mean | 5.5 | 2.6 | 4.1 | 1.3 | | |

When crude palm oil was a traded commodity, the average age at loading was about 6 weeks. The oil was then subjected to an ocean voyage of variable length and to a variety of handling expertise. In transit, the particulate iron went into solution, became more reactive and assumed its well documented prooxidant role, as shown in Table VI.

This oxidation in transit earned palm oil the reputation of being a relatively difficult oil to process, usually with special reference to color and bleachability. Here is another deviation at least from soybean oil. Whereas processing problems with soybean oil are usually reflected in flavor and to a lesser extent color, with palm oil processing defects are reflected as color fixation or reversion.

CAROTENOIDS

The second minor component of major interest to the palm

| TABLE | V | I |
|-------|---|---|
|-------|---|---|

Effect of Storage in Presence of Iron

| Storage condition | | PV (Mg/kg) | A ^{1%} A ²³³ | A ^{1%} AC269 | Carotene (ppm) | Total tocopherol | Lovibond red after scopa |
|-------------------|--------|---------------|-------------------------------------|--------------------------|-------------------|---------------------|--------------------------------|
| Fresh | A B | 1,2 1.5 | 1.10 | 0.22 0.22 | 635 638 | 761 742 | 1.5 1.3 |
| 20 days at 60 C | A | 22.3 | 3.99 | 0.35 | 544 | 605 | 2.4 |
| | B | 36.8 | 5.47 | 0.78 | 85 | 17 | 5.5 |
| 26 days at 60 C | A | 33.1 | 5.35 | 0.35 | 416 | 476 | 3.4 |
| | B | 44.5 | 6.35 | 0.85 | 19 | 10 | 8.1 |

A = oil as such

B - oil with 8 ppm added iron

oil processor is the carotenoids. Present to the extent of 500-700 ppm, the compounds contained within this portion of saponifiables contain α -, β - and γ -carotene, xanthophyl and lycopene.

 α - and β -carotene constitute ca. 91% of the fraction while the other components are represented more or less equally (See Table VII). This group of compounds is responsible for the deep orange red color of crude palm oil.

It is increasingly obvious that with physical refining, color reduction at the bleaching stage is unimportant, since the temperatures required to distill the free fatty acids satisfactorily are sufficiently high to bleach the carotenoids thermally (See Fig. 2). In fact, some refineries only remove 20% of the color of the carotenoid content of the crude palm oil at the bleaching step.

The problem of the final color of processed oil is not one of inefficient removal of the carotenoids. The final color appears to be associated with other pigments or, more likely, the precursors of pigments arising through oxidative deterioration. It has been shown by Wong that oxidized carotene produced no appreciable color on thermal bleaching, neither did oxidized fatty acids.

However, when the carotene and fatty acid were cooxidized, significant color was obtained during thermal bleaching.

There are indications in the literature that other oils attain high final colors at deodorizer temperatures if the earth bleaching step is too aggressive, e.g., excessive temperature or excessive time or both or access to oxygen. The trend in Malaysia is for bleaching temperatures to be reduced to 90-110 C — well below the 150 C advocated by several authors. Earth bleaching can be detrimental to final product quality and PORIM is working on "bleaching" situations where the earth is no more than an "absorptive cleanser" as propounded by Paterson (6), rather than a bleaching agent.

Another disadvantage of overbleaching is that oxidized fatty acids are degraded and there is an appearance of con-

TABLE VII

Palm Oil Unsaponifiable - Carotene Fraction

| Unsaponifiable matter | | | | |
|-----------------------|----------|--|--|--|
| Compound | Quantity | | | |
| α-Carotene | 29% | | | |
| β-Carotene | 62% | | | |
| γ-Carotene | 4% | | | |
| Xanthophylls | 3% | | | |
| Lycopene | 2% | | | |



FIG. 2. Thermal destruction of β -carotene (5).

jugated triene fatty acids. Recent work at PORIM has shown that it is also possible to obtain unusual tocopherol moities (possibly dimers or decomposition products) which may be picked up by high pressure liquid chromatography (HPLC). Bleaching under adverse conditions can, therefore, give rise to a number of artifacts about whose identity little is known and about whose effects even less is known.

If thermal bleaching in the deodorizer or steam refining unit is too aggressive, other problems may arise. Recent work by BFMIRA at Leatherhead has shown that at elevated deodorizer temperatures, unsaturated oils such as soybean or rapeseed oils exhibit conjugation, isomerization and randomization. These effects are shown in Figure 3.

With a less unsaturated material, such as palm oil, this should be of lesser significance. There is, however, a recommendation in Germany that an oil subjected to temperatures



FIG. 3. Effect of heat treatment on fatty acids in soybean (7).

of 270 C and above for times in excess of 30 min should be regarded as being suspect for consumption.

Tocopherols

Overvigorous conditions at deodorizing also lead to a major loss of the other main minor constituent – the tocopherols. About 800 ppm of tocopherols are present in palm oil. The tocopherols in palm oil are a mixture of ca. 20% α -tocopherol, 25% α -tocotrienol, 45% γ -tocotrienol, and 10% δ tocotrienol. Not only are they natural antioxidants, but the

TABLE VIII

Tocopherol Loss in Process

tocopherols group are also physiologically active as vitamin E. Their loss in process is, therefore, to be avoided. It should be stated that at their usual level in palm oil, their presence is not prooxidant as is their much higher level in soybean oil.

Their loss in process is to some extent unavoidable, but actual loss seems to depend on the refiner and to a greater extent on the type of plant he uses, as shown in Table VIII.

Free Fatty Acids

The final minor component of interest to this processor is the free fatty acid level. Initially important as a trading quality standard being the major source of calculable loss, improvements in mill operation mean that the historic standard of 5% FFA is somewhat outdated. However, dissolved iron contents of the oil vary directly with the crude oil FFA, due to dissolving in storage, as does the partial glyceride content with its various implications for the end user.

Palm oil is a semisolid fat with a mean IV 53.3 and a mean slip point 36 C. Its saturated:unsaturated fatty acid ratios being ca. 50:40:10 saturated:monoenoate:dienoate. By virtue of this triglyceride composition, palm oil lends itself to fractionation.

Fractionation per se is not a new process, but in Malaysia the scale to which the operation is practised is unique.

As indicated in Table IX, there are three basic types of fractionation plants, each tending to give a stearin whose characteristics are slighly different from that given by the others. In operation, each plant is similar in that crystallization is effected by means of carefully controlled seeding conditions.

In the wet system, the crystals of stearin are preferentially wetted by a surfactant, normally sodium lauryl sulphate, resulting in higher yields of olein (up to 85% has been claimed) and consequently a much harder stearin.

In the dry system, no additives are used. The oil which can be crude, part processed or fully processed is cooled under controlled conditions and filtered.

In the solvent system the same operation is performed, except that the material being cooled is a miscella, i.e., the

| Refiner | Crude | Neutralized & bleached | Degummed & bleached | Deodorized | Retention (%) |
|---------|-------|---------------------------|------------------------|------------|------------------|
| A | 796 | 744 | | 673 | 84.5 |
| В | 906 | 698 | | 652 | 72.1 |
| С | 841 | | 841 | 554 | 64.6 |
| D | 1103 | | 861 | 478 | 43.3 |
| E | 811 | | 727 | 548 | 67.2 |
| F | 892 | | 838 | 503 | 56.4 |
| G | 824 | | 905 | 628 | 76.2 |

TABLE IX

Daily Palm Oil Fractionation Capacity

| | | | | - | | | |
|---------------------------------------|-------------------|----------|---------|-----|-------|---------|-------------------|
| | Wet Alfa-Laval | | Dry | | | So | lvent |
| | | Tirtiaux | De smet | СМВ | Other | Acetone | Hexane |
| Number of plants Approximate daily | 34 | 8 | 11 | 2 | 2 | 1 | 2 |
| capacity (tons) | 4555 | 2500 | 1600 | 400 | 450 | 200 | None operating |

oil to be fractionated and an organic solvent (usually hexane but can also be acetone, isopropanol or 2-nitropropane).

In Malaysia, solvent fractionation plants initially installed used hexane. At the time of writing it is understood that no plant using hexane is now in operation in Malaysia.

Examination of the fatty acid composition (Table X) shows that the oleins produced in Malaysia fall into a relatively narrow range of iodine values (56.1-60.6) with a mean value of 58.0. As may be expected, the stearins produced fall into a much wider range of iodine values (21.6-49.4). It should be noted, however, that the maximum allowed iodine value for the export of stearin from Malaysia has now been reduced to a maximum of 46, at which iodine value the likely slip melting point will be 47.6-48 C.

The various types (hardnesses) of the stearin are shown in Figure 4.

The hardest stearins (i.e., those having the lowest iodine values) tend to be produced by surfactant fractionation plants. During the fractionation process, impurities tend to be concentrated in the stearin fraction, while desirable components such as tocopherols and carotene tend to be concentrated in the olein, as shown in Table XI. The result is that palm olein has become a favored, stable frying medium for many applications and has even replaced its parent, palm oil, in many instances.

The relative instability of palm stearin is the subject of a PORIM research project. It is probably caused by the impurities in the stearin and the effects of the higher temperatures required to handle this material. Impurities which accumulate are from phospholipids and tocopherol degradation products.

With increasing interest in cocoa butter replacers, many refiners are attempting to produce a satisfactory middle melting fraction from palm oil which will be more or less compatible with cocoa butter. This fraction rich in POP triglycerides is usually obtained by double fractionation. However, POP-rich fractions from these plants require further processing to make them acceptable to the confectionery industry, and they then usually require blending with SOS rich fractions from shea or illipe oils.

If fractionation is from solvent in the first instance, then the preferred solvent is acetone, since crystallization from hexane results in the concentration of partial glycerides in the desired crystalline fractions and the stearin fraction may be difficult to free from occluded olein. When crystallizing from an acetone miscella, partial glycerides are collected in the olein at the expense of cloud point.

Many refiners are now attempting to produce a satisfactory middle melting fraction from palm oil. PORIM has been analyzing the products as shown in Table XII.

TABLE X

| Percentage Fatt | y Acid Composition | of Palm Oil | Oleins and | Stearins (8) |
|-----------------|--------------------|-------------|------------|--------------|
|-----------------|--------------------|-------------|------------|--------------|

| Fatty and | Palm oil | Oleins | Stearin | |
|--------------|----------|----------------|---------|-----------|
| composition | mean | Range observed | Mean | observed |
| 12:0 | 0.2 | 0.1-1.1 | 0.1 | 0.1-0.6 |
| 14:0 | 1.1 | 0.9-1.4 | 1.0 | 1.1-1.9 |
| 16:0 | 44.0 | 37.9-47.7 | 39.8 | 47.2-73.8 |
| 16:1 | 0.1 | 0.1-0.4 | 0.2 | 0.05-0.2 |
| 18:0 | 4 5 | 4.0-4.8 | 4.4 | 4.4-5.6 |
| 18:1 | 39.2 | 40.7-43.9 | 42.5 | 15.6-37.0 |
| 18:2 | 101 | 10.4-13.4 | 11.2 | 3.2-9.8 |
| 18:3 | 0.4 | 0.1-0.6 | 0.4 | 0.1-0.6 |
| 20:0 | 0.4 | 0.2-0.5 | 0.4 | 0.1-0.6 |
| Iodine value | 0.1 | | | |
| (WIJS) | 52.9 | 36.1-60.6 | 58.0 | 21.6-49.4 |



FIG. 4. SFC/temperature profile of palm stearins (9).

TABLE XI

Fate of Minor Components of Fractionation

| Component | СРО | Stearin | Olein |
|-------------------|------|---------|-------|
| Carotene (ppm) | 589 | 347 | 682 |
| | 551 | 268 | 623 |
| Tocopherols (ppm) | 736 | 251 | 796 |
| | 635 | 358 | 904 |
| | 842 | 370 | 994 |
| Phosphorus (ppm) | 17.6 | 27.9 | 4.5 |
| | 14.6 | 43.1 | 5.7 |

As a result of this extensive survey and contacts with the using industry, the current proposed definition of a "midfraction" is a fat which meets the analytical criteria, shown in Table XIII.

TABLE XII

Fatty Acid Compositions of some Malaysian Middle Fractions

| Fatty acid | Refiner | | |
|------------------------|---------|------|------|
| | Α | В | С |
| 10:0 | | | |
| 12:0 | 0.1 | 0.2 | 0.2 |
| 14:0 | 0.9 | 1.0 | 0.9 |
| 16:0 | 51.3 | 47.1 | 46.9 |
| 16:1 | | _ | - |
| 18:0 | 6.3 | 4.7 | 52 |
| 18:1 | 35.2 | 37.2 | 36.9 |
| 18:2 | 5.5 | 9.2 | 9.5 |
| 18:3 | 0.1 | 0.3 | 0.2 |
| 20:0 | 0.6 | | _ |
| Iodine value | 40.7 | 46.7 | 48.9 |
| Slip melting point (C) | 32.6 | 37.3 | 28.9 |

TABLE XIII

PMF Criteria

| PMF Criteria | | | |
|-------------------------|-------|--|--|
| Parameter | Value | | |
| $C50/(C_{48} + C_{54})$ | ≥4 | | |
| C ₅₂ | >43 | | |
| lodine value (WIJS) | 32-55 | | |
| Slip melting point (C) | 23-40 | | |

These may seem wide limits, but the range of middle fractions available simply with these parameters and accepted SFC profiles depends on the type of process used.

Palm oil has for many decades been used as an extremely stable frying medium - stability being due to only 10-11% linoleate and trace quantities of linolenate. Hydrogenation and winterization are not required for stability.

Palm oil has a tendency, when included in margarine formulations, to undergo posthardening. This effect which limits palm oil's use in packet and other margarines is the subject for research project. The effect appears to be due to low rate of nucleation rather than a low rate of crystallization.

Being a semisolid with a slip melting point of 37 C, palm oil readily lends itself for shortenings and other consistent fat formulations - even more so when its rate of nucleation is fully understood. Nucleation notwithstanding, palm oil is a versatile oil whose supply is increasing annually, whose uses are being expanded and whose continued place in the world of fats and oil will be at least maintained.

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