Minor Components from Palm Methyl Esters

Choo Yuen May and Ab. Gapor Md. Top

Crude palm oil contains about 1% of minor components among which the three most important groups are carotenoids, vitamin E (tocopherols and tocotrienols), and sterols. The others are phospholipids, glycolipids, triterpene alcohols, terpenic hydrocarbons, triterpene ethers, wax esters, phenolics and paraffinic hydrocarbons. Among the hydrocarbons, the most abundant is squalene. The quantities of these minor components in crude palm oil (and also in palm fatty acid distillate) are shown in *Table 1,* while detailed carotene, tocopherol and tocotrienol and sterol profiles are shown in *Tables 2, 3* and *4.* The carotenoids, α-tocopherol, tocotrienols and sterols are valuable compounds as they possess significant physiological and medicinal properties (Ong *et al.*, 1990). The carotenes, which are precursors of vitamin A, impart a distinctive orange-red colour to palm oil and together with the tocopherols and tocotrienols contribute to the stability and nutritional value of the oil. The carotenoids, particularly α-carotene, β-carotene and lycopene, are efficient quenchers of singlet oxygen, thus partly explaining their anti-oxidant properties. Recent research findings have associated dietary intake of β-carotene with protection against some types of cancers. Tocopherols and tocotrienols have antioxidant as well as vitamin E activity. A recent report shows that α-tocopherol is a major chain-breaking lipid-soluble antioxidant in mammalian tissues and there is evidence that it may be involved in the division of normal and cancerous cells (Burton and Ingold, 1981; Burton and Ingold, 1986). The tocotrienols have even more interesting physiological properties. For example, α-tocotrienol can suppress elevation of the cholesterol level in blood (Qureshi *et al.*, 1986) and γ-tocotrienol can prevent aggregation of platelets in blood (Holub, 1987) besides having anticancer properties in experimental animals

TABLE 1. MINOR COMPONENTS IN CRUDE PALM OIL (CPO) AND PALM FATTY ACID DISTILLATE (PFAD)[a]

	CPO (ppm)	PFAD (ppm)
Carotenoids	500 - 700	-
Tocopherols and Tocotrienols	600 - 1000	2900 - 7880[b]
Sterols	360 - 620	1540 - 19810[c]
Phospholipids	5 - 130	
Glycolipids	1000 - 3000	
Triterpene alcohols (unsaponifiable)	40 - 80 (estimated)	
Triterpene alcohols (unsaponifiable)	640	
Methylsterols (unsaponifiable)	40 - 80 (estimated)	
Squalene	200 - 500	2400 - 13500[d]
Sesqui-and di-terpene hydrocarbons	*ca* 30	*ca* 500
Aliphatic alcohols (unsaponifiable)	*ca* 100 - 200(160)	
Aliphatic hydrocarbons	*ca* 50	4000 - 8000
Methyl esters	*ca* 50	*ca* 4000
Methyl ketones		*ca* 100
Wax esters	Trace	

[a]Except where otherwise indicated, data are from Goh *et al.*, 1985.
[b]Ab.Gapor (1989) [d]Ab.Gapor *et al.* (1985)
[c]Ab.Gapor *et al.* (1987)

TABLE 2. CAROTENE PROFILE OF CRUDE PALM OIL[a]

Carotenes	Composition (%)
Phytoene	1.27
Cis-β-Carotene	0.68
Phytofluene	0.06
β-Carotene	56.02
α-Carotene	35.06
cis-α-Carotene	2.49
ζ-Carotene	0.69
γ-Carotene	0.33
δ-Carotene	0.83
Neurosporene	0.29
β-Zeacarotene	0.74
α-Zeacarotene	0.23
Lycopene	1.30
Total Carotenes (ppm)	500 - 700

[a]Choo *et al.* (1990)

TABLE 3. TOCOPHEROL (T) AND TOCOTRIENOL (T3) PROFILE OF CRUDE PALM OIL[a]

T + T3	Composition (%)
α-T	22
α-T3	20
γ-T3	46
δ-T3	12
Total T + T3 (ppm)	600 - 1000

[a]Hashimoto *et al.*, (1980).

TABLE 4. STEROL PROFILE OF CRUDE PALM OIL[a]

Sterols	Composition(%)
β-Sitosterol	59.7
Stigmasterol	11.4
Campesterol	23.9
Cholesterol	1.9
Unknown	3.1
Total sterols (ppm)	210 - 620

[a]Siew (1990)

(Kato *et al.*, 1985). Palm oil is a cholesterol-free oil, according to the criterion of the Food and Drug Administration of the USA that, any material containing less than 25 ppm of cholesterol is considered cholesterol-free. However, other sterols are present, *e.g.* β-sitosterol, which has the beneficial effect of being hypocholesterolemic.

Most of the palm oil and palm oil products exported from Malaysia are in processed forms. During physical refining of crude palm oil (CPO) to produce refined, bleached and deodorized (RBD) palm oil or palm oil products, the carotenoids are destroyed and the free fatty acids present are distilled off and collected as a by-product called palm fatty acid distillate (PFAD). Significant amounts of tocopherols, tocotrienols, sterols and squalene are also distilled over and collected in PFAD.

The recovery of carotenoids, tocopherols, tocotrienols and sterols from CPO and PFAD has been found possible after the removal of glycerides and fatty acids as methyl esters. This route outlined below is found to be the most convenient and practical one. It is also economically attractive, as the methyl esters can also be used as feedstock in the manufacture of oleochemicals.

CAROTENOIDS, VITAMIN E AND STEROLS FROM CRUDE PALM OIL METHYL ESTERS

In the conversion of crude palm oil and crude palm stearin into methyl esters using the process developed in PORIM (Choo and Goh, 1987; Choo and Ong, 1987; Choo *et al.*, 1988; Choo *et al.*, 1990), carotenoids, tocopherol, tocotrienols and sterols are found to remain intact in the crude methyl esters. The process has been scaled up to pilot plant and the methyl esters pilot plant located in PORIM is shown in *Figure 1*. It has been demonstrated that carotenes can be recovered either via the distillation of methyl esters or adsorption. The former method, employing molecular distillation in the last stage, has led to concentrates with about 80 000 ppm of carotenes (Ooi *et al.*, 1988). The technical feasibility of this method, has also been proven on a pilot plant scale. The second method, involving adsorption, has led to >90% recovery of carotenes at a concentration of 8000 - 9000 ppm (Choo *et al.*, 1987). The adsorbent can be reused more than 30 times without any loss of activity.

Tocopherol, tocotrienols and sterols, can be recovered by adsorption from the residue remaining after the distillation of the methyl esters. *Table 5* gives an indication of the amounts of these minor components (and of the carotenoids) present in the distillation pot, as well as in a concentrate obtained by silica gel column chromatography. Other recovery methods are also being explored.

The carotene concentrate obtained by the molecular distillation method has been successfully presented in various forms namely capsules, powder and emulsion (Choo *et al.*, 1989) as shown in *Figure 2*.

VITAMIN E, STEROLS AND SQUALENE FROM PALM FATTY ACID DISTILLATE METHYL ESTERS

As stated earlier, PFAD is rich in useful minor components such as vitamin E, sterols and squalene. As PFAD is a relatively

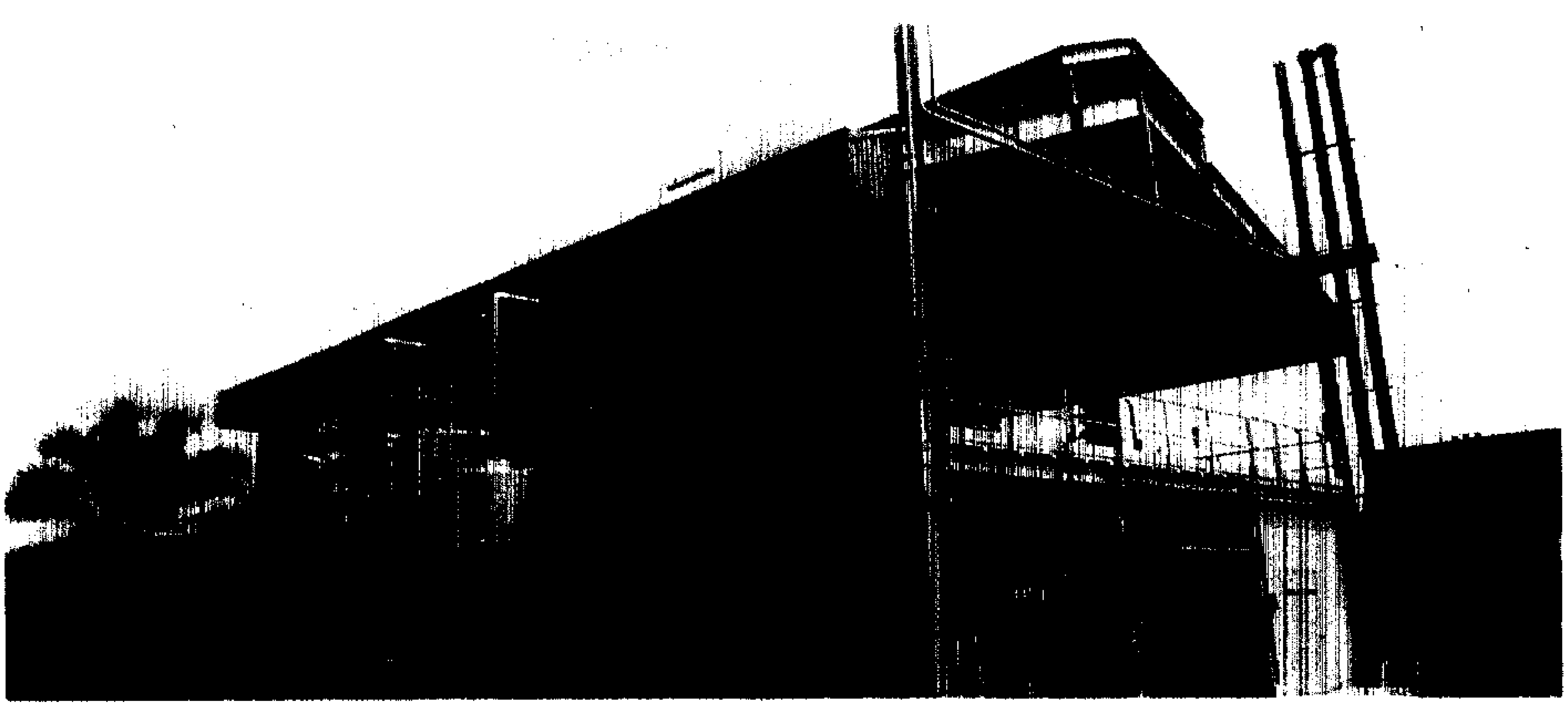

Figure 1. Methyl Esters Pilot Plant

TABLE 5. CONCENTRATION OF CAROTENOIDS, TOCOPHEROLS, TOCOTRIENOLS AND STEROLS AT VARIOUS STAGES IN THEIR ISOLATION FROM METHYL ESTERS

Samples	Carotenoids (ppm)	Tocopherols and Tocotrienols (ppm)	Sterols (ppm)
Neutralized palm oil (NPO)	645	520	not measured
Crude Methyl Esters (ME) from NPO	700	545	860
ME residue[a]	20 780	27 470	not measured
Concentrate of minor components[b]	84 390 (41%)[c]	374 980 (83%)[c]	320 090 (81%)[d]

[a]After vacuum distillation.
[b]Obtained by column chromatography.
[c]Percentage recovery from NPO.
[d]Percentage recovery of sterols from crude methyl esters.

Figure 2. Forms of Carotene Concentrates

low value commodity, PORIM has embarked on an R&D programme on utilizing the material for the recovery of value-added minor components via the methyl ester route. While the R&D on developing a suitable technology for the recovery of sterols and squalene is still at the laboratory stage, on vitamin E it has progressed to the pilot plant stage. A collaborative project between Bioindustry Development Centre - Ministry of International Trade and Industry, (BIDEC-MITI), of Japan and PORIM has resulted in the setting up of a vitamin E pilot plant in PORIM (*Figure 3*) and a joint application for patents for the

Figure 3. Vitamin E Pilot Plant

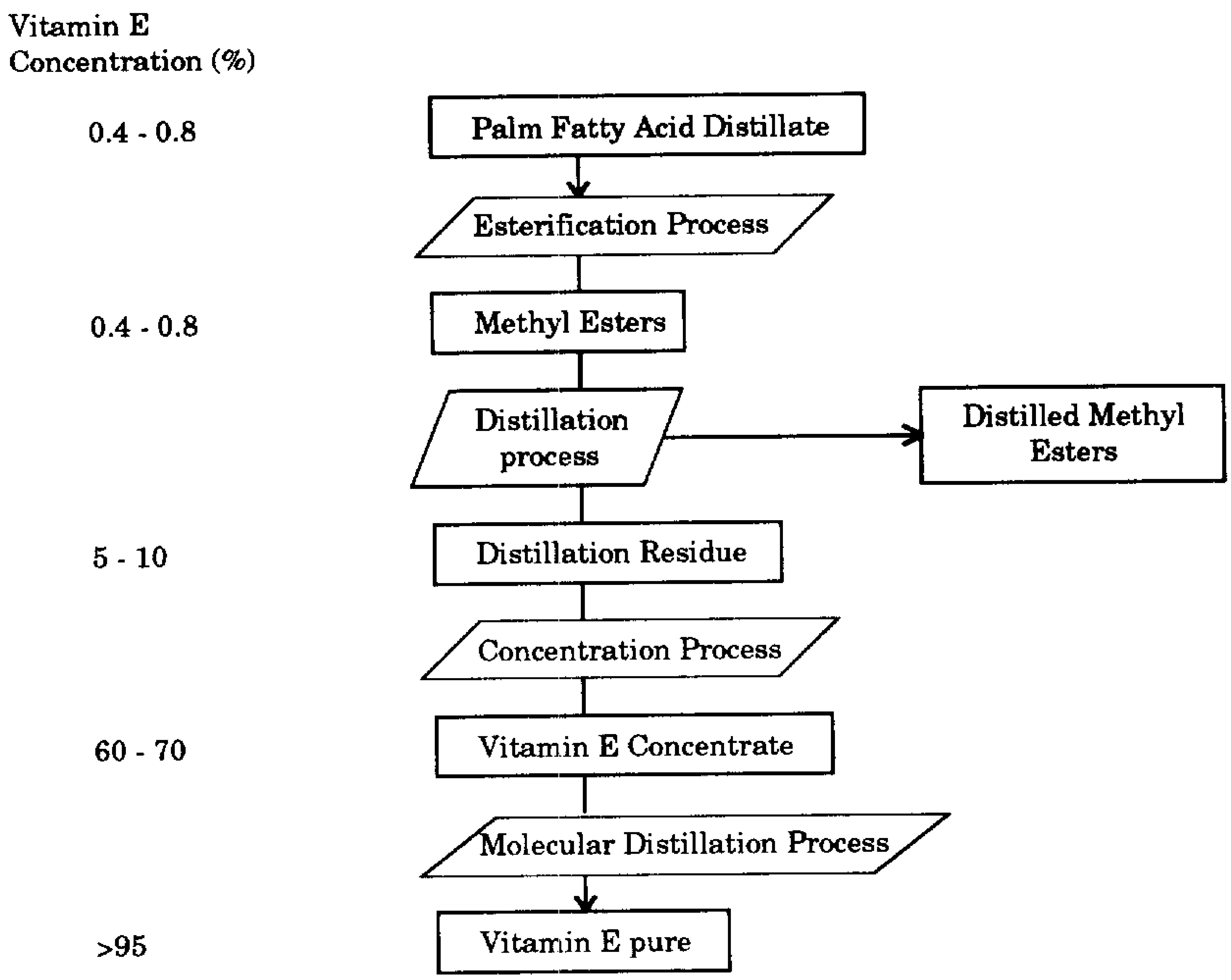

Figure 4. Production Process for Vitamin E

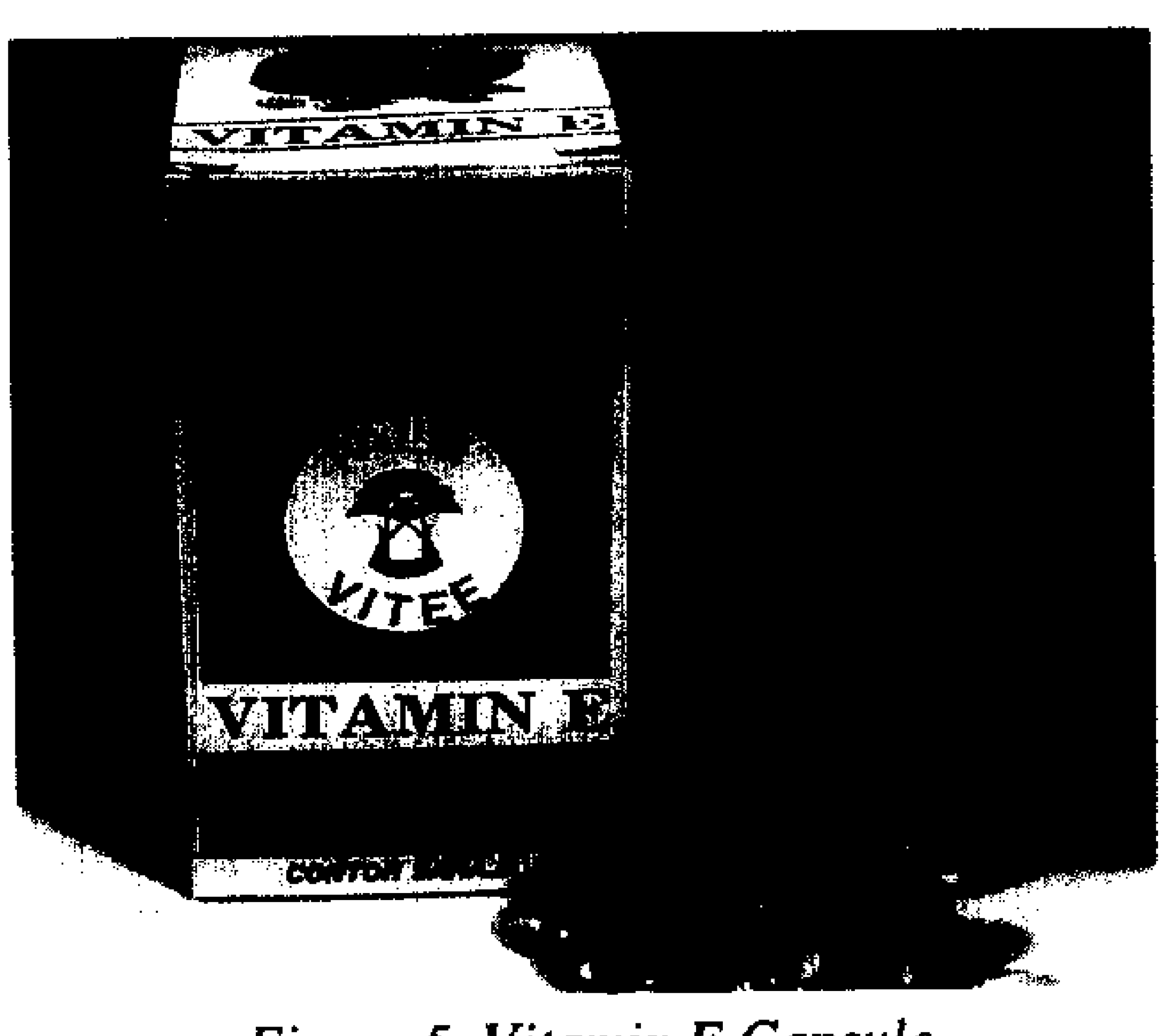

Figure 5. Vitamin E Capsule

production of pure vitamin E (Gapor *et al.*, 1988). A schematic production process for vitamin E (> 95% purity) is given in *Figure 4*. The vitamin E product from the pilot plant has been encapsulated and the capsules have been named PALMVITEE (*Figure 5*). These capsules are used for various promotional and nutritional research activities locally and overseas.

CONCLUSION

The potential for commercializing the production of α-tocopherol and tocotrienols (vitamin E) and carotenoids(α-and β-carotenes) from palm oil and palm oil by-products has been demonstrated. Scientific evidence from nutrition research indicates that these minor components from palm oil can be used as food supplements and pharmaceuticals.

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