8. Coenan, J.W.E., Rev. Franc. Corps Gras 21:343 (1974).
9. Deffense, E., and A. Tirtiaux, Paper presented at AOCS World Conference, The Hague, Holland, October 1982.
10. Haraldsson, G., Paper presented at seminar, Kuala Lumpur, Malaysia, 29th April, 1978.
11. Thomas, A.E., and F.R. Paulicka, Chemistry and Industry, 774, 18th September, 1976.
12. Sonntag, N.O.V., Bailey's Industrial Oil and Fat Products, 1982, 4th Edn. Volume 2, 97.
13. Sreenivasan, B., JAOCS 55:796 (1978).
14. Coleman, M.H., and A.R. Macrae, U.K. Patent 1,577,933 (1980).
15. Macrae, A.R., JAOCS 60:291 (1983).
16. Hernqvist, L., B. Herslöf, K. Larsson and O. Podlaha, J. Sci. Food Agric. 32:1197 (1981).
17. D.G.F. Review, Fette Seifen Anstrich. 75:467 (1973).
18. Madsen, J., Paper presented at A Margarine and Yellow Fats Seminar, Grindsted Products A/S, March, 1983, Coventry, U.K.
19. Tirtiaux, A., and E. Deffense, Paper presented at the AOCS Meeting, Dallas, Texas, U.S.A., May 1984.
20. Young, F.V.K., JAOCS 60:374 (1983).
21. Wiegand, E., et al., Federal Republic Germany Patent 1,910,062 (1969).
22. Kattenberg, H.R., and C.C. Verburg, U.S. Patent 4,055,679 (1977).
23. Teasdale, B.F., and G.A. Helmel, U.S. Patent 3,174,868 (1965).

Fractionation of Palm Oil

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ABSTRACT

Because of its fatty acid composition, which includes 50% saturated and 50% unsaturated fatty acids, palm oil can readily be fractionated, i.e. partially crystallized and separated into a high melting fraction or stearin and a low melting fraction or olein.

Three main commercial processes for fractionating palm oil are in use: the fast dry process, the slow dry process and the detergent process. All these processes lead to specific products of different quality with different yield and operating costs. The physical and chemical characteristics as well as the triglyceride compositions by high performance liquid chromatography (HPLC) of palm oil fractions from these industrial fractionation processes are given.

Other varieties of products produced by specific fractionation are presented with analytical data: the superoleins, palm-mid-fractions and cocoa butter substitutes.

INTRODUCTION

The task of presenting this paper about fractionation of palm oil is far from simple, especially when I have to stand as judge and party to the subject. I have therefore chosen to restrict this study to a qualitative and—I hope—objective picture of palm oil fractions as it stands in 1984. I thank PORIM and the Malaysian and Indonesian refiners as well as the equipment manufacturers for supplying documentation and samples.

Out of a world production of around 6.4 million metric tons (MT) in 1983, over 2 million tons of palm oil are fractionated in the tropical countries like Malaysia, Indonesia, Ivory Coast and Colombia. Most fractionation plants have been established in Malaysia over the last decade, thanks to the development policy of the Malaysian government.

Palm oil as *Eleais guineensis*, with an iodine value of around 53 and a saturated:unsaturated fatty acid ratio of 50:50, is a semi-solid oil, sedimenting at room temperature even in tropical countries. Therefore, a fractional crystallization is required.

Because of its triglyceride composition which includes substantial quantities of both low and high melting point triglycerides, palm oil can readily be crystallized by controlled cooling and separated into a low melting fraction, olein, and a high melting one called stearin.

In this paper emphasis is placed on the physical and chemical characteristics of palm oil fractions with regard to the methods of fractionation currently in use. Later we will talk about the specific fractions such as superolein and palm-mid fractions.

Two main processes for fractionating palm oil are in commercial use, differing in the separation step (Fig. 1).

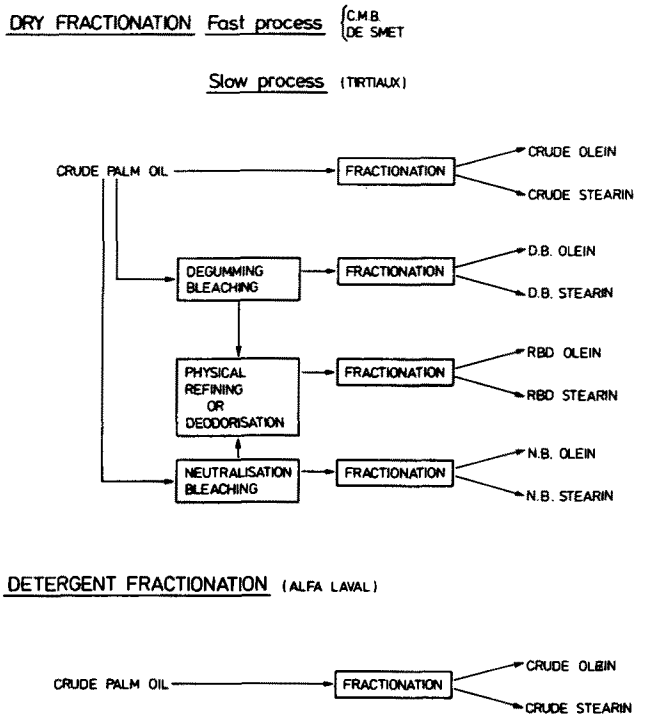

FIG. 1. Integration of fractionation process in the refining cycle.

The dry process uses direct filtration of the crystals, and the detergent process uses an aqueous detergent solution to separate the crystals from the olein by centrifugation. As can be seen from Figure 1, palm oil in this case is fractionated crude, since the olein and stearin will require full refining to remove traces of detergent.

A third process, not developed here, in which crystallization is done in solvents and followed by filtration, has been almost abandoned due to high operating cost, except for the production of cocoa butter replacers as discussed later.

FRACTIONATION PROCESSES

Dry Fractionation

The dry fractionation processes, available commercially and representing the largest production, include Bernardini, Extraction de Smet for the fast dry process and Fractionnement Tirtiaux for the slow dry process.

Bernardini (C.M.B.) (1,2). In the C.M.B. process, palm

oil is cooled in a batch crystallizer fitted with 3 thermoregulated water tanks at different temperatures. The water from each tank is made to circulate in sequence for a preset period of time. In semi-continuous version, palm oil is agitated for a pre-established time into 4 crystallizers thermoregulated from 35 down to 16 C.

The filter is a "radial" filter where separate filter elements radiate out from a slowly rotating horizontal shaft dipped in the filter chamber in which the palm oil slurry is kept at a constant level. Vacuum is applied to the elements of the filter which become submerged in the liquid phase and olein is sucked, leaving a coating of stearin on the surface which is expelled from the filter leaves by compressed air.

Extraction De Smet (3). The fundamental principle of the De Smet process is also a rapid cooling of the melt to produce crystals of stearin. A preliminary cooling of oil is achieved to reach the temperature at which nuclei are formed. The oil is then cooled to 19 C in a crystallizer provided with a very large cooling surface in comparison with the volume of oil treated. "This ensures total exchange with a very small differential temperature between oil and cooling medium."

Filtration is achieved by means of a Stockdale type rotary filter in which the cooled palm oil is fed into a bottom tray in contact with the filter cloth. A vacuum sucks in the olein and the stearin sticks to the filter cloth to be cleared subsequently by strings or a scraper.

Fractionnement Tirtiaux (4,5,6). The first commercial plant to fractionate palm oil was set up by Tirtiaux in 1969 in Bogota. The principle of cooling is a patented process whereby it is the temperature of the oil that actually controls the rate of cooling. Unlike other processes, the oil is crystallized relatively slowly to control the latent heat of crystallization and to avoid supercooling.

The oil is fed into agitated crystallizer tanks fitted with coils and jackets in which the crystals are melted and then allowed to form and grow.

The filter used is the Florentine filter developed by Tirtiaux. The filtration takes place horizontally on an endless rotating stainless steel belt under a slight vacuum. The filter is self-cleaning, and the filtration area is enclosed and air conditioned. Thus the oil mixture is maintained at temperature of fractionation until the olein is separated from the stearin. A recycling device enables the filtrate from the first filter belt section to be recycled. This results in filtrating on a preformed stearin cake and in increasing the quality of the filtrate.

TABLE I

C.M.B. Oleins and Stearins from Single Stage Fractionation

Palm oil	RBD					
Origin	Indonesia		Malaysia			
Process			Continuous		Batch	
Fraction	Stearin	Olein	Stearin	Olein	Stearin	Olein
Code	239		231-2		231-3	
Iodine Value (GLC)	44.3	57.1	46.7	58.0	47.8	58.6
Yield (%) (calc.)	37	63	40	60	40	60
Slip melting point (C)	48.6	24.5	48.2	24	47.7	23
SFC (%) by pulsed NMR						
5 C	75.9	52.8	75.3	54.7	74.2	48.3
10 C	68.6	36.9	66.7	37.0	65.8	36.4
15 C	59.2	19.9	55.5	17.4	53.9	18.6
20 C	47.6	3.0	44.0	3.0	42.2	2.2
25 C	36.0		32.4		30.0	
30 C	26.1		23.4		21.4	
35 C	18.5		16.2		14.3	
40 C	13.1		9.5		8.3	
45 C	8.0		5.7		4.3	
50 C	2.1		.8		–	
55 C	–		–		–	
Fatty acids (% wt as Me)						
C 16:0	51.4	40.4	49.3	39.5	48.4	39.0
C 18:0	4.7	4.3	4.9	4.3	4.9	4.4
C 18:1	32.8	41.1	33.8	41.5	34.5	41.7
C 18:2	8.7	11.9	9.6	12.2	9.9	12.4
Diglyceride (% wt)	5.1	6.2	5.2	6.9	5.5	6.8
Triglyceride (% wt)	94.9	93.8	94.8	93.1	94.5	93.2
Triglyceride composition (area %) by HPLC						
S_3	19.5	.4	17.3	.5	16.0	.4
S_2U	46.4	50.0	45.9	48.2	45.8	48.0
SU_2	30.0	42.8	31.6	44.3	33.0	44.5
U_3	4.1	6.8	5.2	7.0	5.2	7.1
Cloud point (C)[a]	–	10	–	10.1	–	9.6
Cold test at 22 C[b] (days)	–	1	–	1	–	2

[a]Cloud point (AOCS Cc-6-25).
[b]Cold test (AOCS Cc-11-53).

Detergent Fractionation

Alfa Laval (7,8). Developed earlier by Lanza and later by the Henkel group, the Alfa-Laval Lipofrac system was the first detergent palm oil fractionation plant set up in Malaysia.

The process consists of chilling palm oil in the presence of detergent and magnesium sulfate (10-20%) to a temperature of 20 C, at which additional detergent solution or wetting agent consisting of sodium lauryl sulfate combined with magnesium or sodium sulfate is added. When the cooled and partially crystallized oil is mixed with a detergent solution, the crystals (stearin) are wetted by the detergent and pass into suspension in the aqueous phase.

The mixture then can be separated by a centrifuge into a liquid oil phase (olein) and a water phase (stearin). The olein mixture is washed with water to remove excess detergent and then dried. The stearin is melted and then centrifuged to separate it from the detergent solution. It is subsequently washed and dried.

ANALYTICAL DATA

The main objective of fractionating palm oil is to obtain olein of low cloud point for cooking oil or further processing into cocoa butter replacer (CBR). The stearin is used as a component of harder frying fats or for the production of shortening, margarine and vanaspati.

More sophisticated fractions as superoleins and palm mid fractions are produced increasingly but have little in common with current oleins and stearins. Therefore we will review them separately.

Olein and Stearin Fractions from Single Stage Fractionation

Eighty-two samples of olein and stearin obtained from the main commercial processes were analyzed in the Tirtiaux analytical laboratory for their chemical and physical characteristics. It was chosen to restrict the comparison of samples to these 82 in order to eliminate discrepancies which may occur from analyses made in different laboratories. For the reader's benefit, many other data are available from publications by PORIM (9,10). Tables I, II, III, IV summarize the results. All the fractions analyzed were taken from industrial plants in Southeast Asia, from palm oil having around the same Iodine Value (52-53), except those from Indonesia where palm oil has a lower I.V. (51).

Fatty acid compositions. The fatty acid compositions of the oleins and stearins plotted against iodine values are shown in Figure 2, giving stearins on the left and oleins on the right. As can be observed, the palmitic acid tends to migrate in the stearin while the fatty acid composition of triglycerides of palm oil and that of oleins remains relatively similar in spite of fractionation.

The normal arbitrary criterion for an olein is that its cloud point should be below 10 C. The cloud point refers to the temperature at which an olein turns cloudy when the oil is cooled at a rate of 1 C per min. In order to pass this specification, most of the oleins produced in Malaysia fall into a relatively narrow range of iodine values (56-58) with an average value of 40, 42 and 11, respectively, for the palmitic, oleic and linoleic acid.

On the contrary, the stearins fall into a wide range of iodine values (25-49). They can be graded into three types (hard, medium-hard and soft grade) covering three ranges of melting: 56-53 C for detergent process, 51-50 C for slow dry process and 49-46 C for fast dry process.

Solid Fat Content by Pulsed NMR (Bruker PC 20)

This wide range of compositions is reflected in the three different ranges of solid content profiles shown in Figure 3: the hardest stearins with the lowest iodine value are produced by the detergent process. The two other types come from the dry processes. For comparison the SFC curves of palm oil and oleins also are shown.

TABLE II

De Smet Oleins and Stearins from Single Stage Fractionation

Palm oil	RBD			
Origin	Malaysia			
Fraction	Stearins		Oleins	
Code	237-B	236-1	237-B	236-1
Iodine value (GLC)	44.9	48.7	57.6	58.4
Yield (%) (calc.)	37	40	63	60
Slip melting point (C)	48.8	45.9	24.2	23.3
SFC (%) by pulsed NMR				
5 C	77.2	72.4	55.7	54.1
10 C	69.6	61.9	39.0	36.8
15 C	58.9	50.7	20.0	17.2
20 C	47.5	38.6	2.5	.9
25 C	36.2	27.0		
30 C	26.4	18.1		
35 C	18.9	12.4		
40 C	12.9	6.2		
45 C	8.5	2.0		
50 C	2.2	–		
55 C	–	–		
Fatty acids (% wt as Me)				
C 16:0	50.6	47.4	39.8	39.2
C 18:0	5.2	5.0	4.4	4.5
C 18:1	32.9	35.3	41.4	41.7
C 18:2	9.0	10.0	12.1	12.4
Diglyceride (% wt)	5.3	5.7	6.8	7.0
Triglyceride (% wt)	94.7	94.3	93.2	93.0
Triglyceride composition (area %) by HPLC				
S_3	19.3	13.8	.6	.7
S_2	46.0	46.2	48.1	47.9
SU_2	30.0	34.6	44.6	44.1
U_3	4.7	5.4	6.7	7.3
Cloud point (C)	–	–	10.2	10.3
Cold test at 22 C (days)	–	–	1.5	1.2

Application of High Performance Liquid Chromatography (HPLC) Analysis to Palm Oil Fractionation

Since fractionation affects at first the triglyceride composition rather than the fatty acids composition of palm oil, HPLC can be used to monitor the fractions. HPLC is indeed an efficient and rapid method which separates the triglycerides by chain length and degree of unsaturation (11).

The present analysis, compared with those obtained by Jurriens and Kroesen (12) and Jacobsberg (13) is shown in Table V. The good agreement in the three sets of results reflects the accuracy of the HPLC method, which is fast and simple compared to the existing TLC-GLC method.

Triglyceride Composition by HPLC Versus Iodine Value

By plotting the triglyceride composition by HPLC versus iodine value, a clearer pattern is provided (Fig. 4). The triglycerides have been grouped in terms of saturated (S) and unsaturated fatty acids (U).

The major trend certainly is the variation of the trisaturated glycerides (S_3) which have very high contents for low iodine values. This is reflected in Figure 5, where the

TABLE III

Tirtiaux Oleins and Stearins for Single Stage Fractionation

Origin	RBD Indonesia				Neutralized Malaysia			
Fraction	Stearins		Oleins		Stearin	Olein	Stearin	Olein
Code	229-B	229-A	229-B	229-A	244-B		243-A	
Iodine value (GLC)	39.4	40.4	57.6	58.2	28.6	57.2	40.1	57.2
Yield (%) (calc.)	30	33	70	67	32	68	28	72
Slip melting point (C)	51.4	50.7	23.0	19.9	50.7	22.2	49.7	21.5
SFC (%) by pulsed NMR								
5 C	83.0	82.1	56.0	55.9	80.3	55.7	76.9	58.4
10 C	78.8	77.2	38.9	35.2	76.0	40.0	70.1	39.2
15 C	70.5	68.7	19.8	15.7	6.3	19.3	61.2	19.7
20 C	59.9	58.0	1.8	–	54.7	.2	48.7	.5
25 C	48.9	46.1	–		43.1	–	38.0	–
30 C	38.1	35.0			31.9		28.0	
35 C	28.4	24.2			23.2		19.7	
40 C	21.1	18.3			16.9		14.3	
45 C	15.4	12.3			11.0		9.3	
50 C	7.9	5.9			4.8		3.2	
55 C	–	–			–		–	
Fatty acids (% wt as Me)								
C 16:0	55.5	54.6	40.2	39.4	55.5	39.5	55.2	39
C 18:0	4.9	4.9	3.8	4.0	4.9	4.6	4.9	4.4
C 18:1	29.9	30.7	41.7	42.3	29.1	41.3	29.9	41.7
C 18:2	7.5	7.6	11.8	11.9	7.2	11.7	7.8	11.6
Diglyceride (% wt)	4.3	4.5	6.5	6.7	4.7	6.6	4.6	5.8
Triglyceride (% wt)	95.7	95.5	93.5	93.3	95.3	93.4	95.4	94.2
Triglyceride composition (area %) by HPLC								
S_3	26.5	23.3	.6	–	21.9	.4	20.2	.2
S_2U	44.5	48.1	48.8	47.8	47.0	48.1	45.6	48.7
SU_2	25.4	25.3	44.1	45.4	27.1	44.7	29.7	44.3
U_3	3.6	3.3	6.5	6.8	4.0	6.8	4.5	6.8
Cloud point (C)	–	–	9.5	6.8	–	8.7	–	8.5
Cold test at 22 C (days)	–	–	2.5	7[a]	–	5	–	2

[a]Minimum.

chromatograms of the three types of stearins (soft, medium-hard, hard) show an increase of the PPS, PPP and MPP peaks with PPP alone rising from 10 to 18 and 32%. For HPLC conditions see reference (11).

In the oleins, a considerable reduction of S_3 occurs.

The second major tendency is that of the content of monosaturated triglycerides (SU_2) to increase towards the high iodine value. Compared to palm oil, the oleins are enriched in monosaturated triglycerides, SU_2.

In contrast, the disaturated class, S_2U, remains fairly close to that of palm oil. Of the disaturated triglycerides (SSU and SUS) the assymmetrical isomer crystallizes in the stearin while the symmetrical isomer occurs more in the olein due to the intersolubility effect.

The last class, the triunsaturated glycerides (U_3) is hardly different from that of palm oil except in hard stearins.

Now for the oleins of 56-58 iodine value, let us consider the inter-relationship between the triglyceride composition and the physical properties such as the cloud point and the cold stability, which are tightly bound.

The first observation is that the presence of S_3, even in a low amount, is quite detrimental to the cloud point and to the low temperature stability because it may initiate a post crystallization.

It appears that the SU_2 glycerides, mainly POO, improve the cloud point. As can be seen, a high value is observed for oleins from slow dry process while a low value is registered for oleins from detergent process. Oleins from fast dry processes have intermediate values.

On the other hand, S_2U is higher in the oleins from detergent process, due probably to the passage of olein through the centrifuge which raises the temperature of the olein slightly due to the frictional force. This would result in the remelting of that part of S_2U that crystallizes at the critical temperature of 20 C.

U_3 glycerides which can be considered as a solvent are fairly constant in oleins from dry processes but lower in detergent process oleins.

It appears that, due to a lower S_2U content and a higher SU_2 content, the slow dry process gives oleins of a better cloud point. This result also can be amplified by the recycling device of its filter. For example, a N.B. palm olein of 8.6 C cloud point can be reduced by recycling to 7.8 C. The analysis in this case shows that the S_2U content has decreased from 47.6 to 46.3 and the SU_2 content has increased from 44.7 to 46.3%.

Distribution of Minor Components of Palm Oil

As palm oil contains about 94% triglycerides, other minor components are present. It appears that most of them—

TABLE IV

Alfa Laval Oleins and Stearins from Single Stage Fractionation

Palm oil	Crude					
Origin	Indonesia		Malaysia			
Fraction	Stearin	Olein	Stearins		Oleins	
Code	230		223-2	234-1	223-2	234-1
Iodine value (GLC)	24.9	58.0	28.0	34.6	57.8	57.8
Yield (%) (calc.)	20	80	17	23	83	77
Slip melting point (C)	55.9	19.0	55.3	53.8	21.7	19.9
SFC (%) by pulsed NMR						
5 C	92.0	49.2	91.4	86.9	54.4	53.2
10 C	92.1	32.7	90.0	81.9	34.4	34.9
15 C	90.8	9.2	84.9	76.2	14.6	13.4
20 C	86.6	–	79.8	68.6	.6	–
25 C	78.0		71.5	57.3		
30 C	68.2		61.6	46.6		
35 C	57.0		51.8	37.8		
40 C	46.0		41.9	29.9		
45 C	35.8		32.2	23.0		
50 C	25.0		22.5	13.0		
55 C	9.3		7.9	.4		
Fatty acids (% wt as Me)						
C 16:0	68.8	40.0	66.2	60.1	39.4	39.6
C 18:0	5.1	4.3	4.8	5.1	4.3	4.4
C 18:1	19.1	40.8	21.6	26.0	42.3	41.7
C 18:2	4.5	12.3	5.0	6.6	11.3	11.8
FFA (mol wt 256) (%)	2.2	3.9	2.2	2.3	4.3	3.5
Diglyceride (% wt)	3.6	6.5	2.8	3.9	6.0	5.2
Triglyceride (% wt)	96.4	93.4	97.2	96.1	94.0	94.8
Triglyceride composition (area %) by HPLC						
S_3	46.1	.2	42.0	32.9	.3	.1
S_2U	43.9	50.9	41.4	45.5	50.2	50.1
SU_2	9.2	43.2	14.2	19.0	43.2	43.7
U_3	.8	5.7	2.4	2.6	6.3	6.1
Cloud point (C)	–	9.8	–	–	10.9	8.7
Cold test at 22 C (days)	–	4	–	–	3	7

TABLE V

Triglycerides Composition of Palm Oil

Number of double bonds	Triglyceride	Jurriens & Kroesen (1965) Sumatra		Jacobsberg (1975) Malaysian		Present results (1984) Malaysian
0	PMP	.3	.9	.5	.7	.7
	MPP	.6		.2		
	PPP		6.1		4.8	6.1
	PPS	.9	1.2	.8	2	1.5
	PSP	.3		1.2		
	Others		.3		.3	
Subtotal			8.5		7.9	8.3
1	MOP		1.1		1.0	–[a]
	POP	25.9	31.9	28.7	32.2	30.9
	PPO	6.0		3.5		
	POS	3.1	3.9	4.7	5.8	5.4
	SPO	.3		.3		
	PSO	.5		.8		
	SOS	–			.3	.5
	Others		.8		.4	–
Subtotal			37.7		39.7	36.8
2	MOO	–	22.0	.4	21.3	22.1
	POO	18.9		19.6		
	OPO	1.2		.5		
	PLS	1.9		1.2		
	SOO		2.6		1.8	2.4
	PPL	1.7	8.5	.9	7.8	10.7[a]
	PLP	6.8		6.9		
	MLP		–		.3	.6
	Others		1.9		.9	–
Subtotal			35		32.4	35.8
3	OOO	3.2	3.7	3.3	3.8	3.5
	SLO	.5		.5		
	SOL		2.6		.1	
	MOL			5.5	10.7	10.7
	POL		4.3	4.8		
	PLO		.5	.4		
	OPL		.6		.1	–
	Others					
Subtotal			11.7		14.8	14.2
4	OOL	1.5	2.8	1.9	2.7	1.8
	OLO	1.3		.8		
	PLL		2.6	1.4	1.5	2.7
	LPL		–	.1		
	SLL		.5		.1	–
	LLO		–		–	.5
Subtotal			6.9		5.1	5.0

[a]MOP and MOO are included in the PPL-PLP peak.

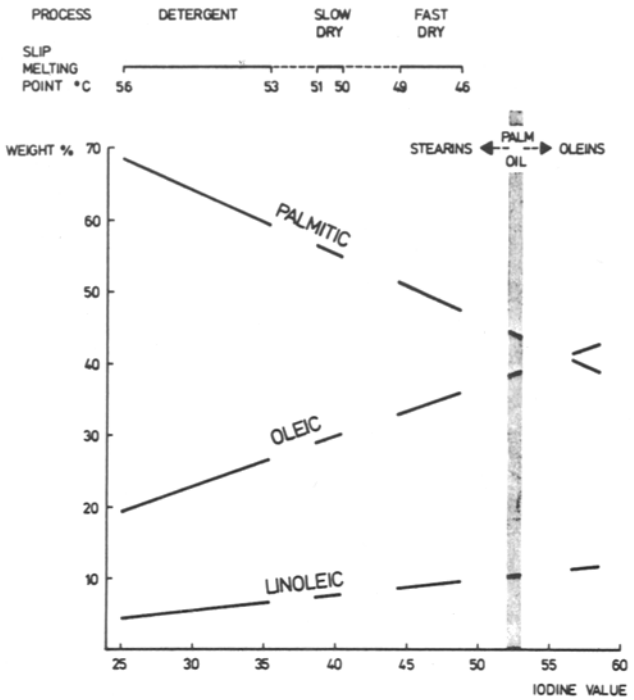

FIG. 2. Fatty acid composition versus iodine value from single stage fractions of palm oil.

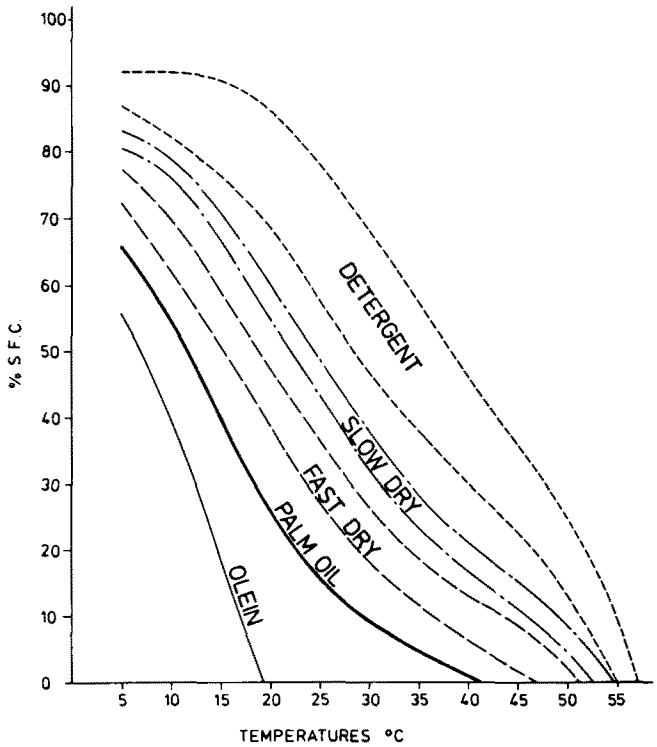

FIG. 3. Solid fat content of palm oil stearins.

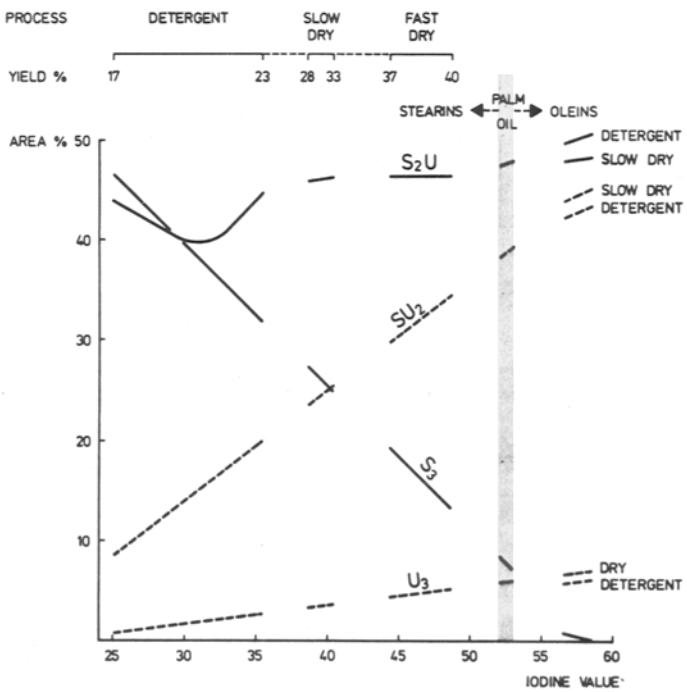

FIG. 4. Triglyceride composition by HPLC versus iodine value from single stage fractions of palm oil.

fatty acids, diglycerides, carotene, sterols, tocopherols, peroxides and oxidized products—remain preferentially in the olein except phospholipids and metals like iron, which migrate predominantly to the stearin.

Main Characteristics of Fractionation Processes

The main characteristics of the fractionation processes may be summarized as in Table VI.

The detergent process consists of a fast crystallization of crude palm oil giving small crystals cleaned by detergent. As a result, the olein yield is high (77 to 83%).

In dry processes, bigger crystals generally are required for the filtration, and as a result the crystals tend to group together in clumps which will occlude part of the liquid phase. This results in a lower yield (60 to 72%). This occlusion, which also is reflected in the SFC of stearins shown above (Fig. 3), is only partly responsible for a yield decrease of around 10%. A lower olein yield also should be

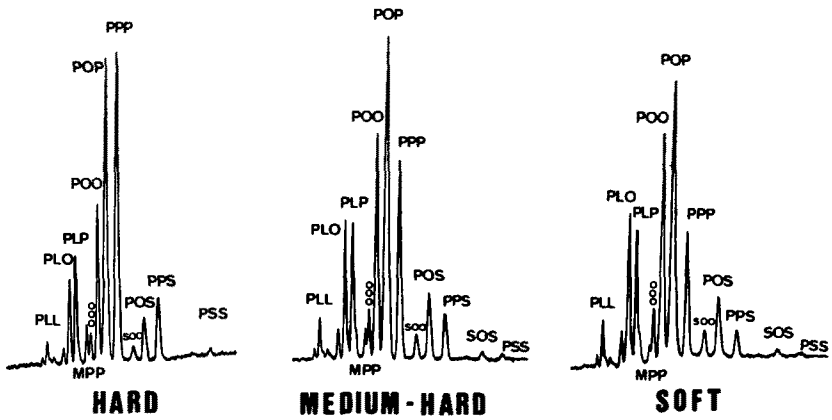

FIG. 5. HPLC chromatograms of palm oil stearins.

attributed to the intersolubility and the formation of mixed crystals (14).

However, if the cooling is controlled properly at a slow rate, like in the slow dry process, the separation and the yield (68-72%) are found to be better, whereas a fast cooling will tend to crystallize the unsaturated molecules with saturated ones.

Other parameters also play a role in the yield, such as the incoming oil quality and the type of refining treatment.

When a high olein yield is of highest importance, which is occasionally the case for palm oil in exporting countries like Malaysia, the detergent process may be the best. In these cases, however, the use of membrane filter presses in conjunction with a dry crystallization process now seems to give yields comparable to those of the detergent process. However, production with these types of filters is still too small and samples too scarce to include results in this paper.

SPECIFIC FRACTIONS

Two other types of products are produced by specific fractionation. The first range of products is that of super olein of lower cloud point. The second type is that of palm mid-fractions as cocoa butter replacers.

These two ranges of products are generally obtained by double fractionation.

Super Olein

When the target is to produce an olein for temperate and cool climates, the required specifications usually are a cloud point below 5 C and a minimum iodine value of 60. Such oleins also are blended with a more unsaturated oil such as soybean oil to improve the low temperature stability.

The analytical data of three super oleins chosen for the study are shown in Table VII.

Compared to an olein from single stage fractionation, the super olein is characterized by the absence of trisaturated glycerides (S_3), an increase of about 8% of the monosaturated triglycerides content (SU_2) and a decrease of about 10% of the disaturated triglycerides content (S_2U).

TABLE VI

Main Characteristics of Fractionation Processes

Process	Fast dry	Slow dry	Detergent
Palm oil	Crude, semi & fully refined		Crude
Olein			
Yield %	60-63	67-72	77-83
Cl. point C	9.6-10.2	8.5-9.5	9.8-10.9
Cold test 22 C (days)	1-2	2-5	3-4
SFC at 20 C	1-3	0.02-1.8	0.6
Stearin			
Type	Soft	Medium-Hard	Hard
Investment cost	Lower		Higher
Operating cost	Lower		Higher
Additives	No		Yes
Effluent treatment	No		Yes
Possibility of separation at T°	Possible	Easy	Difficult

Yield calculated on feedstock basis.
CPO oleins have lower SFC due to the FFA content.

TABLE VII

Super Oleins from Double Stage Fractionation

Code		16	342	276
Iodine value (GLC)		60.7	62.9	62.7
Slip melting point (C)		18.2	16.0	15.0
SFC (%) by pulsed NMR				
5 C		57.0	48.1	39.6
10 C		33.5	23.7	10.3
15 C		7.9	1.9	.3
20 C		–	–	–
Fatty acids (% wt as Me)				
C 16:0		37.3	35.6	34.9
C 18:0		4.1	4.0	3.7
C 18:1		43.8	44.2	46.9
C 18:2		12.3	13.4	12.1
Diglyceride (% wt)		–	6.3	9.4
Triglyceride (% wt)		–	93.7	90.6
Triglyceride composition (area %) by HPLC				
S_3	PPP	–	–	.2
S_2U	POS	4.8	3.4	3.0
	POP	24.8	23.0	21.3
	PLP	11.7	11.9	11.0
	MLP	.6	.6	.4
SU_2	SOO	3.7	3.4	4.0
	POO	30.1	31.7	33.8
	PLO	13.2	14.7	14.2
	PLL	4.1	3.6	2.7
U_3	OOO	4.9	4.8	6.1
	OOL	2.2	2.3	2.8
	LLO	–	.6	.5
Cloud point (C)		5.1	4.8	5.7
Cold test at 16 C (hrs)		40	54	44

TABLE VIII

Palm Mid-Fractions from Double Stage Fractionation

NO	A	B	C	CBS	CBS
Code	92	255	243	266-A	266-B
Iodine value (Wij's)	40.3	45.2	49.9	35.9	35.4
Diglycerides (% wt)	4.8	5.6	4.1	2.5	4.3
Triglyceride composition (% wt) by GLC					
C 46	1.1	.8	.5	.6	.7
C 48	6.5	5.0	3.5	4.3	4.6
C 50	61.1	55.8	50.6	68.5	70.5
C 52	25.7	30.9	36.3	21.2	19.7
C 54	5.4	7.4	8.6	4.9	4.0
C 56	.2	.2	.5	.4	.3
$\frac{C\ 50}{C\ 48 + C\ 54}$	5.1	4.5	4.2	7.4	8.2
Triglyceride composition (area %) by HPLC					
PPS	1.0	.7	.2	.6	.3
PPP	4.8	2.6	1.5	2.3	2.0
MPP	.9	.7	.4	.5	.3
SOS	1.1	1.6	.6	3.1	1.5
POS	9.2	8.5	7.5	14.1	13.3
POP	55.1	49.0	43.1	64.4	69.2
MOP	1.1	1.2	1.2	1.3	1.2
PLP	8.0	8.7	9.1	7.5	7.5
MLP	.1	.2	.6	–	–
SOO	1.2	1.6	1.8	.5	.2
POO	11.1	15.3	18.8	3.9	3.4
PLO	3.9	5.8	8.6	1.0	1.1
PLL	.6	.7	2.3	.1	–
OOO	1.4	2.3	2.6	.6	–
OOL	.6	.9	1.3	–	–
LLO		.2	.4	–	–
S_3	6.7	4.0	2.1	3.4	2.6
S_2U	74.6	69.2	62.1	90.4	92.7
SU_2	16.7	23.4	31.5	5.5	4.7
U_3	2.0	3.4	4.3	.6	–
Slip melting point (C)	33.8	33.3	28.6	32.5	33.4
SFC (%) by pulsed NMR					
5 C	80.8	75.6	71.1	93.7	93.4
10 C	80.1	67.7	60.3	88.0	88.3
15 C	72.9	57.7	45.8	80.9	82.3
20 C	58.7	42.4	26.2	69.4	68.7
25 C	28.7	16.6	4.0	31.3	26.8
30 C	11.5	6.4	.4	5.4	5.4
35 C	5.0	1.3	–	.6	.3
40 C	.6	–	–	–	–

These tendencies are still amplified when the olein is fractionated in solvent as shown in Figure 6, but the cloud point is not necessarily better due to the higher concentration of diglycerides in solvent processed oleins.

Palm Mid-fraction

Unlike super olein, palm mid-fraction is characterized by a high disaturated triglycerides S_2U content—greater than 50%—and a low monosaturated triglyceride SU_2 content —lower than 30% (Table VIII).

A first remark, if we compare the diagram of Figure 6 with that of first fractionation (Fig. 4), we observe a total inversion of the distribution of the disaturated triglycerides (S_2U), which increase towards low I.V., i.e. towards mid-fractions.

Palm mid-fraction, which is used as cocoa butter substitute (C.B.S.) or as the main component (50-70%) of confectionery fat as the cocoa butter equivalent (C.B.E.), should exhibit properties similar to those of cocoa butter. In other words, the fraction should be high in monounsaturated triglycerides as POP and should have a short melting range.

The analytical criteria of a mid-fraction presently defined by PORIM (15) in conjunction with the industry in Malaysia are as follows:

PMF criteria

Parameter	Value
Ratio $\frac{C\ 50}{C\ 48 + C\ 54}$	4 minimum
C 52	43 maximum
I.V. (WIJ's)	32-55
Slip melting point C	23-40

If we look at the Figure 6, which shows the triglyceride

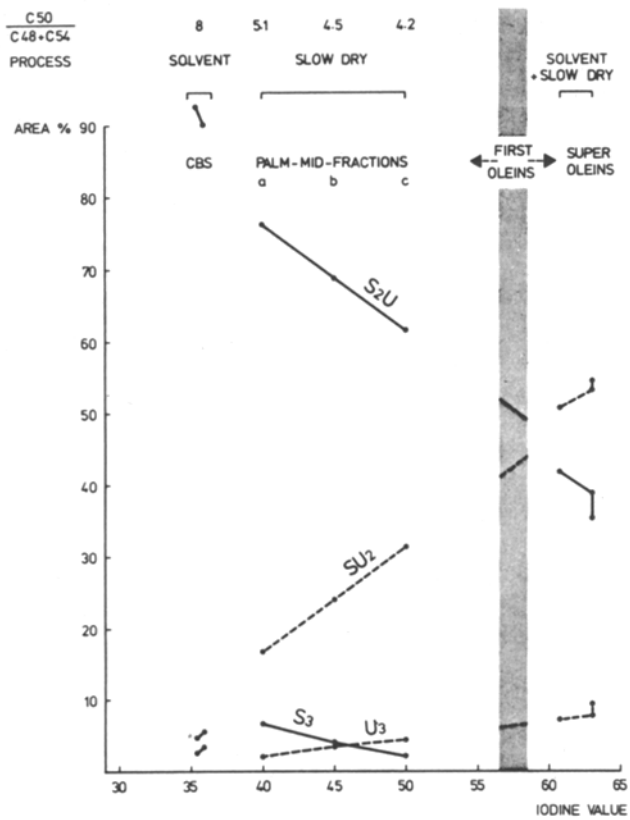

FIG. 6. Triglyceride composition by HPLC versus iodine value from double stage fractions of palm oil.

composition by unsaturation versus iodine value of three commercial PMF A, B, C made with a slow dry process, they fit in quite well with these specifications: the iodine value ranges from 40 to 50, the slip melting point varies from 33.5 to 28.6 C and the C 50/C 48 + C54 ratio is higher than 4.

However, if we compare these fractions with two European CBS obtained by double fractionation of palm oil in acetone, we understand that these POP rich fractions require further processing to make them acceptable to the confectionery industry. These products must be treated by single stage solvent fractionation in order to eliminate the unsaturated triglycerides.

When looking at the HPLC chromatograms displaying the triglyceride composition (Fig. 7), one can realize that fractionation should be done with the objective of concentrating oleodipalmitin (POP), oleopalmitostearin (POS) and oleodistearin (SOS) with a minimum amount of undesirable triglycerides like tripalmitin (PPP) which are difficult to eliminate in further solvent fractionation. On the other hand, unsaturated glycerides like palmitodiolein (POO) linoleooleopalmitin POL can be removed easily by solvent fractionation to give products such as C.B.S.

These tendencies also are reflected in the solid content profiles shown in Figure 8.

The C.B.S., having an SFC fairly similar to that of cocoa butter, is characterized by a big drop in solid content from 20 C to 30 C and is melted completely at 35 C (requisite characteristic of coating fats).

Compared to palm oil, the three PMF analyzed have a steep solid content profile but, compared to C.B.S., their solid content is lower at low temperature especially when POO increases at the expense of POP. However, a high PPP content leads to a high melting tail, difficult to correct in a

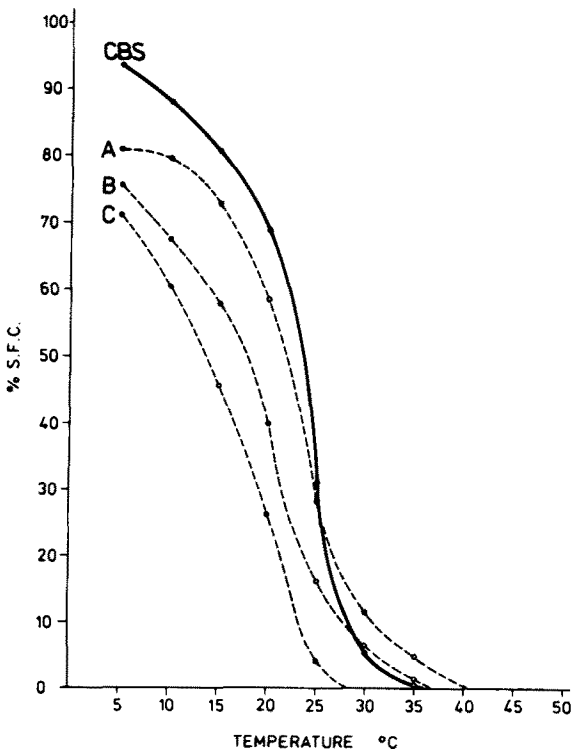

FIG. 8. Solid fat content of palm mid-fractions.

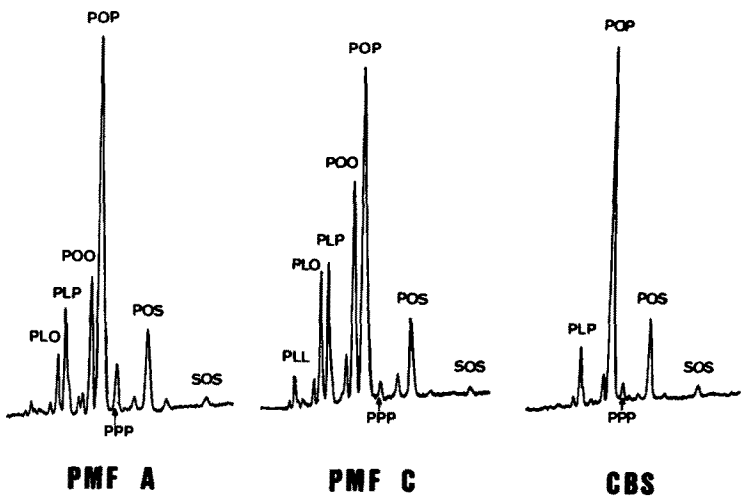

FIG. 7. HPLC chromatograms of palm mid-fractions and CBS.

later fractionation by solvent.

To conclude, I would like to recall that the crystallization is a dynamic reaction where the molecules of triglycerides are in equilibrium. Many parameters such as the oil composition, the temperature, the polymorphism and the intersolubility may influence this equilibrium. Therefore, depending on the crystallization method used, the quality as well as the yield of the fractions will be affected.

The availability of palm oil fractions has given opportunity for greater adaptability to specific requirements.

The palm oil fractions from single and double stage, blended or not with other oils, followed or not by interesterification, may give new markets. As striking examples we find the superoleins and especially the palm mid-fractions where throughput and cost consideration are of less importance for the high value product.

REFERENCES

1. Bernardini, M., and R. Sassoli, Palm Oil Fractionation with C.M.B. Process, Palm Oil Technology in the Eighties, Kuala Lumpur, 1981.
2. Bernardini, M., Technical literature, Rome, Italy.
3. Athanassiadis, A., Refining and Segregation of Palm Oil, AOCS meeting, St. Louis, Missouri, 1978.
4. Tirtiaux, F., Oleagineux 31:279 (1976).
5. Tirtiaux, A., and E. Deffense, Tirtiaux Fractionation–Industrial Application and Analytical Data, AOCS meeting, The Hague, The Netherlands, October 1982.
6. Tirtiaux, A., Technical literature, Fleurus, Belgium.
7. Braae, B., Detergent Fractionation of Fatty Oils, Proceedings of the Symposium of the Belgian Filtration Society, Brussels, 1976, pp. 189-210.
8. Haraldson, G., The Alfa-Laval Lipofrac Process for Fatty and Acids, Seminar in Kuala Lumpur, April 1977.
9. Tan, B.K., and F.C.H. Oh, PORIM, Technology No. 4, 1981.
10. PORIM Technical Brochure, Malaysian Palm Oil Refining Industry, 1981.
11. Deffense, E., Rev. Franç. Corps Gras, 31:123 (1984).
12. Jurriens, G., and A.C.J. Kroesen, JAOCS 42:9 (1965).
13. Jacobsberg, B., Oleagineux, 30:271 (1975).
14. Deroanne, C., Contribution à L'étude de la Cristallisation des Glycérides, Dissertation (1975).
15. Tan, B.K., F.C.H. Oh, S.H. Ong and K.G. Berger, Characteristics of Malaysian Palm Mid-fractions, PORIM report, 1981.

Fractionation of Lauric Oils

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ABSTRACT

The different methods of edible oil fractionation are reviewed, and the applicability of these to the fractionation of palm kernel and coconut oils is discussed. Crystallization from solvents such as acetone, hexane or 2-nitro-propane, is the most easily understood and most convenient for small-scale laboratory trials, but the cost of solvents and the need to flameproof plants makes it uneconomical for an industrial undertaking. Dry crystallization is commonly employed, and there are several methods, described here, for subsequent separation of solid stearin from liquid olein. Chemical and physical properties of the separated stearins and oleins depend on fractionation conditions and on the yields sought. These are reviewed. The properties of the fractions may be further modified by hydrogenation, interesterification, blending or combinations of these techniques.

Many sophisticated confectionery fats are manufactured from lauric stearins and their methods of manufacture and product applications are reviewed. A commercial operation must take care to find a good outlet for the secondary fractionation products (or byproducts) however, and useful outlets for these secondary fractions are therefore considered in addition to those of the main product.

INTRODUCTION

Lauric fats are obtained from various species of palm tree, the two main varieties being palm, which produces palm kernel oil, and coconut. There are in addition several minor varieties of lauric fat such as babassu, tucum and ouri-curi, but as these are seldom encountered except in the country of origin, and often have specific properties, they will not be considered in this paper. I will therefore concentrate on the fractionation of palm kernel and coconut oils.

Palm kernel and coconut fats differ from nonlaurics in that they contain 47-48% lauric acid, together with smaller amounts of other medium- and short-chain fatty acids. This gives the fats a solid consistency at cool ambient temperatures, but they nevertheless melt below 30 C. Typical fatty acid compositions and melting properties are shown in Tables I and II. The natural fats thus have short melting ranges, which suits them to the manufacture of a variety of fatty foods. Lauric oils have therefore been prized for a wide variety of food stuff applications for very many years. Nevertheless, the fats' melting points and solid contents at room temperature are a little low for production of confectionery coatings and couvertures, a drawback that can be alleviated by fractional crystallization and separation of the harder and softer components.

The advantages of fractionation were first appreciated

TABLE I

Typical Lauric Fat Compositions

Fat	IV	Fatty acids (wt %)						
		C_6-C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18}:1	C_{18}:2
Palm kernel oil	17.5	7	48	16	9	2	15	2
Palm kernel stearins	9	6	53	21	9	2	8	1
	7	4	55	22	9	2	7	1
	2	3	50	30	12	3	2	0
Palm kernel stearin (IV = 7)	4	4	55	22	9	6	5	0
hydrogenated to lower IV	0.4	4	55	22	9	9	0.5	0
Palm kernel stearin (IV = 7) refractionated to lower IV	3	3	56	26	9	2	3	0.5
Coconut oil	8.5	15	48	18	8	3	6	2
Coconut stearin (25% yield)	4	9	55	22	9	2	3	0.5
Hydrogenated coconut stearin	1.5	9	55	22	9	5	2	0
Palm kernel olein	21	9	45	13	9	3	19	2
Coconut olein	10	17	46	17	7	3	7	3