

Studies in Palm Oil Crystallization

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ABSTRACT

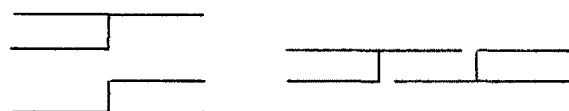
The melting and crystallization behaviors of palm oil were examined by nuclear magnetic resonance, differential scanning calorimetry, and plasticity measurements and were correlated with composition and chemical characteristics. Fractionation into high melting and low melting components is adversely affected by increase in free fatty acids (FFA), diglyceride content, and degree of oxidation, and hence, for an oil that is to be fractionated, both hydrolysis and oxidation should be kept to a minimum. Palm oil with very low FFA content, obtained from ripe, unbruised fruit, contains substantially more diglycerides than would be expected from the level of FFA present. Liquid and solid palm oil fractions manufactured in the producing countries showed large variation in characteristics, due in part to the use of various fractionation processes. The characteristics used to define the quality of palm oil are also applicable to its fractions.

INTRODUCTION

Fatty acids and glycerides show pronounced polymorphic properties in the solid state. This polymorphism has been studied extensively, mainly by Lutton (1,2), on pure substances. Polymorphism is due to the stereochemical configuration of the molecules in the crystal, which for triglycerides assumes an unsymmetrical "tuning fork" pattern (3) with different orientations of the carbon chain zigzag arrangement. It is recognized now that, except for triglycerides containing short chains (C_{12}, C_{14}), fast cooling produces α , and also $\text{sub}\alpha(=\beta'_2)$, which upon heating passes through the following steps: $\beta'_2 \rightarrow \alpha \rightarrow \beta'_1 \rightarrow \beta$ (4). The energy necessary for these transitions is a function of the crystal structure, and thus the transitions from one state to another are fast for even-numbered fatty acids and symmetric triglycerides but slow for uneven-numbered chains and asymmetric triglycerides. The transition rate slows down with increasing chain length.

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X-ray diffraction has shown that each state corresponds to a definite packing order of "short spacing" (i.e., distance between hydrocarbon chains lying contiguously to each other) and "long spacing" (i.e., width of successive layers of contiguously packed molecules). The latter depends on the chain length of the molecule but also on the angle of tilt between a hydrocarbon chain and the boundary plane of the molecular layer (5,6). The melting and solidification of fats is also governed by the degree of intersolubility of the glycerides, which is linked to the pattern of imbrication of the triglyceride chains in the crystal. The most common configurations are of patterns usually called "double chain" and "triple chain":



double chain structure

triple chain structure

Knoester et al. (7) showed in phase kinetics and crystal properties studies of binary mixtures of triglycerides with stearic and palmitic chains that the mixed crystal formation is strongly enhanced by the presence of an asymmetric triglyceride. This means that the intersolubility of the crystals is very high in this case and that the melting range is narrowed. This intersolubility has also been studied by Deroanne (8) in differential scanning calorimetric (DSC) investigations of crude palm oil.

Crystallization can be compared to a chemical reaction insofar as a certain energy barrier has to be overcome to produce molecular clusters which will eventually grow into crystals, and this necessitates supercooling. Depending on the cooling conditions, different polymorphic forms appear. The tendency for polymorphism is quite pronounced in palm oil crystals. This must be ascribed partly to the relatively high amount of symmetric monooleic disaturated triglycerides, similar to cocoa butter composition.

The symmetric/asymmetric dipalmito-olein (POP/PPO) system can also produce a compound with a crystal structure quite distinct from the polymorphic form of the

TABLE I

Effect of Tempering Conditions on Solid Fat Content as Measured by Pulsed Nuclear Magnetic Resonance for Crude Malaysian Palm Oil

Tempering conditions	Sample number	% FFA (mol wt 256)	% Solid fat content					
			15 C	20 C	25 C	30 C	35 C	40 C
(a)	17	2.20	34.6	20.6	12.6	8.1	4.3	2.3
	18	3.34	29.9	17.0	12.7	8.3	5.7	1.8
(b)	17		28.5	16.4	10.0	8.1	4.1	0.4
	18		19.6	12.2	9.3	8.0	4.9	1.9
(c)	17		51.8	41.9	23.1	10.8	4.0	0.9
	18		46.7	41.0	21.9	10.4	4.2	1.6

(a) Sample melted at 60 C, chilled at 0 C for 30 min, then tempered for 30 min at each measuring temperature by stepwise increase. (Chilling at -12 C instead of 0 C did not produce any substantial difference.)

(b) Sample melted at 60 C, tempered at 28 C for 72 hr, chilled for 30 min at -12 C, and then kept for 30 min at each measuring temperature in stepwise increase.

(c) Sample melted at 60 C, chilled for 30 min at -12 C, and then tempered for 72 hr at each measuring temperature.

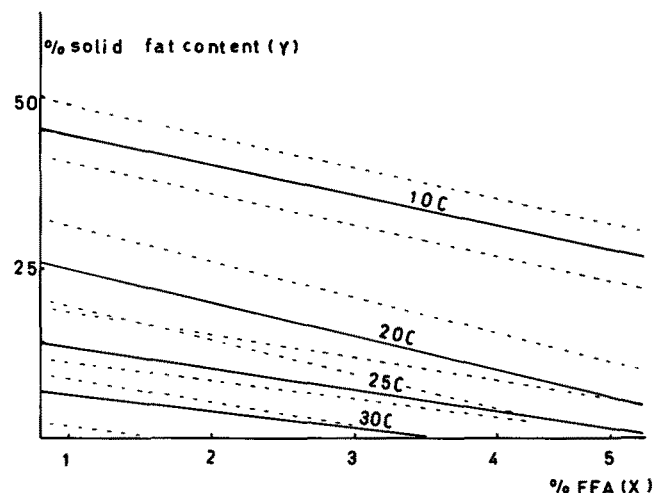


FIG. 1. Effect of the percentage of free fatty acid on solid fat content in crude palm oil (confidence limits for a probability of 90%).

components. Such compounds show eutectic formation, as illustrated by Rossel's isodilatation phase diagrams (9).

Palm oil cooled rapidly and then warmed (at a rate of 0.5 C/min) undergoes three phase transformations according to Persmark et al. (10):

- Below -10 C to -5 C → β'_2 phase (low melting β' phase)
- From -5 C to 7 C → α and β'_1 phase
- Above 7 C → mainly pure β'_1 phase

Slow cooling of the melt leads to β'_1 crystals (high melting β' phase).

Solid fractions of palm oil separated after progressive cooling show much more complex polymorphic properties than those of the original palm oil. Evidently the α -form is predominant after rapid cooling, but Persmark showed also that the lifetime of these α -crystals is considerably increased through the presence of partial glycerides. Also, these partial glycerides and free fatty acids (FFA) decrease the solid fat content by eutectic formation. This is in agreement with Riiner's (11) findings for completely refined sheanut oil from crude oils with various high degrees of hydrolysis, and also with the well-known increase in plasticity for acidified palm oil (12,13). Altogether, it appears that polymorphism, transition rates, and inter-

solubility of the triglycerides, partial glycerides (i.e., di- and monoglycerides), and FFA may have repercussions on a number of important properties of palm oil and especially on fractionation.

The present study is an attempt to investigate crystallization and melting behavior of palm oil with regard to FFA and partial glyceride content, degree of oxidation, origin, and methods of fractionation (samples from industrial fractionation plants).

The following experimental techniques and conditions were applied to measure the crystallization and melting properties:

- Solid fat content determination by pulsed magnetic resonance: For the calibration of the instrument and the measuring techniques, the methods of Van Putte (14,15), Weisser et al. (16), and Geldner (17) were applied with satisfactory results with a Bruker Minispec P 20. The differences between the results of indirect and direct measurements of the solid fat content were below 1.5% and generally ca. 0.5%. Table I illustrates the well-known fact that the tempering conditions produce substantial variations in the solid fat content. The different tempering modes applied showed good reproducibility in solid fat content at the different temperatures.

It is assumed that the tempering close to the measuring temperature (c) increases the solid fat content because of further crystal growth and formation of new crystals. After a tempering at 28 C (b), the results for unfractionated palm oil were lower than expected, i.e., lower than for tempering (a). Close agreement existed between results of direct and indirect measurements. Finally, the DGF tempering method, also used by Van Putte and by Geldner, was adopted. It differs from method (a) only insofar as the samples are cooled in ice for 90 min instead of 30 min.

The pretreatment by crystallization in acetone and petroleum ether proposed by Seher and Werner (18) did not lead to satisfactory reproducibility in the measurements of solid fat content.

- Differential scanning calorimetry was used to record melting and crystallization curves at a heating rate of 8 C/min with a DSC-Perking Elmer-1B.
- Plasticity was measured by cone penetration of an ASTM penetrometer after melting the samples

TABLE II

Characteristics of Palm Oil Samples from the Same Origin Extracted from Unbruised (No. 11) and Bruised (No. 16) Ripe Tenera Palm Fruit: Comparison with Palm Oil from Industrial Production^a

Number	Origin	% FFA (mol wt 256)	Carotene (ppm)	Tocopherol ^b (ppm)	Absorbance ^c		Peroxide value (meq/kg)	Anisidine value
					233 nm	269 nm		
11	Unbruised fruit	0.31	678	556	1.070	0.099	0.1	0.6
12		0.98						
13		1.93						
14		3.11						
15		4.08						
16	Bruised fruit	5.14	616	814	1.168	0.224	0.1	0.1
17	Industrial production	2.20	575	830	1.492	0.298	0.1	1.65
18	Industrial production	3.34	600	841	1.646	0.225	0.5	3.60

^aPrepared by courtesy of Unipamol, Kluang, and MARDI Oil Palm Branch. Samples 12-15 were obtained by mixing samples 11 and 16 in suitable proportions.

^bDiphenyl picryl hydrazyl (DPPH) method for total non-carotene reducing substances.

^cCorrected for carotene.

TABLE III
Crystallization Behavior of Palm Oil from the Same Origin with Increasing FFA Contents:
Comparison with Plantation Palm Oil from Industrial Production

	Number							
	11	12	13	14	15	16	17	18
	% FFA (mol wt 270) ^a							
	0.32	1.03	2.04	3.28	4.30	5.42	2.23	3.52
	Percentage of solid fat content (by pulsed nuclear magnetic resonance)							
Crude palm oil								
15 C	46.9	47.2	45.8	44.2	42.3	40.5	34.6	29.9
20 C	34.5	33.0	30.8	27.1	26.0	23.7	20.6	17.0
25 C	23.9	21.9	21.0	19.2	17.8	16.7	12.6	12.7
30 C	14.0	13.8	13.0	12.4	12.5	11.2	8.11	8.3
35 C	9.1	10.2	9.5	8.7	7.8	7.5	4.3	5.7
40 C	6.3	5.8	5.6	5.3	4.6	3.2	2.3	1.8
Alkali neutralized palm oil (FFA<0.2%)								
15 C	-	47.7	47.1	44.9	46.4	47.7	37.0	35.6
20 C	-	34.3	32.6	29.1	30.4	31.7	21.3	20.3
25 C	-	23.7	22.1	17.0	20.0	21.1	14.3	14.6
30 C	-	15.0	13.1	10.0	11.2	12.7	8.8	9.1
35 C	-	10.0	8.4	5.6	8.4	6.5	7.5	5.6
40 C	-	6.4	5.9	3.7	4.0	5.2	2.2	3.2

^aMean mol wt of fatty acids in palm oil.

TABLE IV
Partial Glyceride Composition of Palm Oil from the Same Origin from Unbruised (11) and Bruised (16) Ripe
Tenera Palm Fruit: Comparison with Samples of Palm Oil from Industrial Production (17 and 18)^a

Sample number	R _f	11	16	17	18
Free fatty acids (mol wt 270) (%)	0.65	0.32	5.42	2.23	3.52
Diglyceride 1,3 (%)	0.50	1.56	4.60	3.18	4.80
Diglyceride 1,2 (%)	0.39	4.10	3.0	2.16	2.95
Monoglycerides (%)	0.06	0.02	0.44	0.44	0.51
Oxidation products and polar unsaponifiable matter (%)	0.00	0.07	0.30	0.33	0.50
Sum of diglycerides (%)		5.66	7.60	5.34	7.75
Ratio $\frac{1,3 \text{ diglycerides}}{1,2 \text{ diglycerides}}$		0.38	1.53	1.47	1.63

^aAnalysis by thin layer chromatography on silica gel 0.25 mm. Elution with 70 vol hexane, 30 vol ethyl ether, 1 vol acetic acid. Revelation with sulfochromic acid and charring at 150 C. Evaluation by densitometry.

completely and cooling them for 16 hr at -12 C and tempering at the measuring temperature for 24 hr.

FACTORS INFLUENCING CRYSTALLIZATION OF PALM OIL

FFA and Partial Glyceride Contents

Our own results corroborate those of Persmark insofar as an increase in FFA and diglyceride contents will decrease the solid fat content, and increase the plasticity of palm oil up to FFA contents of ca. 7%. It was possible to establish a regression equation between the solid fat content and FFA contents for palm oil samples from industrial production (Fig. 1).

To avoid the influence of uncontrolled factors, such as origin, ecology, etc., a series of tests was carried out on palm oil samples of identical origin. These samples were meant to reproduce as closely as possible normal practical conditions. Therefore, several bunches from Tenera hybrid palms were chosen, and the spikelets of ripe, unbruised fruit only were selected and subdivided into two homogeneous lots. One lot was immediately sterilized, whereas the other was first mechanically bruised in order to produce a rise in FFA content to ca 5% through the action of the

fruit lipase and then also sterilized. From both samples the oil was expressed separately by handpress and clarified. By mixing adequate portions of the two oils (0.3 and 5.1% FFA content), intermediate samples were obtained (Table II). For the sake of comparison, two samples of industrially produced palm oils were also examined.

A regular perceptible decrease of solid fat content occurs with increasing FFA content (Table III). After alkali neutralization, however, this trend is much less noticeable, except for the industrially produced samples. The DSC curves showed a slight shift towards the lower melting range, with increasing FFA contents. Elimination of the FFA by alkali refining produces a shift towards a higher melting range.

For plasticity determination also, the general trend was confirmed, but again the differences were less pronounced than expected in the neutralized samples.

Altogether, the influence of the FFA and the diglyceride content on the crystallization behavior was clearly shown. After alkali neutralization, however, the effect of the partial glycerides (diglycerides) alone was not so well marked. This fact must be ascribed to the irregular diglyceride composition of the palm oil samples with very low FFA content from unbruised fruit.

TABLE V
Effect of Oxidation on the Crystallization Behavior of Palm Oil

Number	Characteristics of samples (g)													
	% FFA (mol wt 270)	Monoglycerides (%)	Diglycerides			Absorbance ^a		Carotene (ppm)	Tocopherol ^b (ppm)	Peroxide value (meq/kg)	Anisidine value			
			1,2 (%)	1,3 (%)	2,3 (%)	233 nm	269 nm							
R1	3.50	0.07	2.03	3.51	1.808	0.476	569	717	0.27	5.17				
R2	<0.1	-	1.95	3.44	1.805	0.391	553	668	0.12	1.08				
R3	-	-	-	-	1.086	0.394	617	391	0.03	1.03				
R4	-	-	-	-	5.875	4.886	-	-	3.61	1.20				
R5	-	-	-	-	1.546	0.526	593	341	0.06	7.4				
R6	-	-	-	-	3.345	1.546	462	256	0.34	28.8				
Solid fat content by pulsed nuclear magnetic resonance (%)														
	10	10C	15	15C	20	20C	25	25C	30	30C	35	35C	40	40C
R1	59.8		41.1		30.0		18.6		10.4		5.6		1.1	
R2	65.1		45.4		34.8		21.3		11.5		5.8		0.8	
R3	72.0		49.7		37.3		24.2		11.8		5.9		1.1	
R4	62.8		46.2		35.2		21.8		11.5		5.4		0	
R5	70.3		49.2		37.3		24.1		12.0		6.1		0.1	
R6	67.8		48.8		37.3		23.9		11.5		6.2		0	
Plasticity 1/10 mm ASTM Cone Penetration														
	25	25C	20	20C	15	15C	10	10C	5	5C	0	0C	0	0C
R1	>160		60		32		16		8		4		2	
R2	>160		49		29		15		7		3		1	
R3	121		34		23		12		6		3		1	
R5	104		34		19		10		5		2		1	
R6	128		35		22		11		6		3		1	

^aCorrected for carotene.

^bDiphenyl picryl hydrazyl (DPPH) method.

Diglyceride Content of Palm Oil from Unbruised Ripe Fruit

All the preceding samples (Nos. 11-18) were analyzed for partial glyceride content by TLC on silica gel. The results were quantified by densitometry using the FFAs as internal standards. These results are quite unexpected (Table IV) insofar as palm oil from unbruised ripe fruit with FFA content below 0.3% has a very high diglyceride content, equivalent to an FFA of ca. 2.5%. These high diglyceride contents explain why in the preceding series of tests the influence of the partial glycerides on the crystallization was not more apparent. It is also noteworthy that the ratio symmetric:unsymmetric diglycerides is reversed compared to normally produced palm oil. Hydrolysis of the ester groups due to fruit lipase and chemical splitting is random, as proved by the similar composition of the free and bound fatty acids. One would expect, therefore, that the 1,2-diglyceride content would be about twice the 1,3-diglyceride content. The results however, show a higher 1,3-diglyceride content for normal oils. It has been shown recently that isomerization into the more stable 1,3-diglyceride occurs at temperatures near the melting point (20), and apparently this isomerization takes place already in the oil of bruised fruit.

The composition of palm oil from unbruised fruit was again checked on another series of four samples obtained from four different Tenera bunches. The results were in close agreement with the preceding.

Finally, the influence of the diglycerides on crystallization behavior was more clearly shown by their complete elimination by percolation over silica gel (Table V, samples R1-R3). This showed that the effect of FFA and diglyceride contents is additive in lowering the solid fat content and increasing the plasticity.

Diglycerides are building stones in the triglyceride synthesis *in vivo*, and the source of diglycerides is not only hydrolytic splitting. This suggests that while for favorable crystallization behavior, among other considerations, the FFA content should be kept low, there seems to be no real benefit from the crystallization viewpoint alone to attempt to produce palm oil with FFA contents very much below 2%.

Oxidation

To check the influence of oxidation on crystallization behavior, a sample of triglycerides was prepared from crude industrially produced plantation palm oil, in the following manner:

- R2) Neutralization using Na carbonate
- R3) Percolation over silica gel at 50 C under a nitrogen blanket. This eliminates all polar constituents, partial glycerides as well as oxidation products. The purity of the resulting triglycerides was checked by thin layer chromatography (TLC)
- R4) A portion of these triglycerides was thoroughly oxidized by heating at 80 C for 48 hr in the presence of copper probes
- R5 & R6) Five and 25% of this oxidized oil was then added to portions of the purified triglyceride sample.

All samples were analyzed for chemical composition and crystallization behavior (Table V and Fig. 2). It appears that oxidation products (R4) act in a similar manner as the diglycerides and FFA, insofar as their presence decreases the solid fat content. Plasticity seems not to be affected by these products. But the influence of oxidation is especially apparent in the DSC melting curves. Peak surface increases for pure triglycerides, and addition of the oxidation products flattens the curves (mixed crystal formation?). It is not possible from the data of chemical analysis to deduce the total amount of oxidation products in the samples.

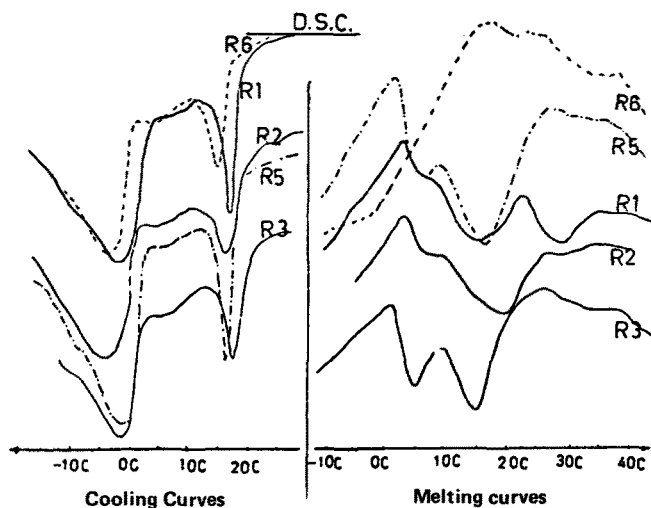


FIG. 2. Differential scanning calorimetry: Effect of free fatty acids, diglycerides, and oxidation products on palm oil crystallization.

However, the oxidation values are not too far removed from those which can be encountered in practice. It can be safely assumed from the present figures that protection from oxidation, besides other beneficial effects on the quality, will also improve the crystallization properties of palm oil.

Origin

Plantation palm oil samples from different countries were analyzed for solid fat content (Table VI). All these samples, except the one from Dahomey, came directly from the production centers. The solid fat content is very similar for all the samples, except the Dahomey oil, which has a substantially higher FFA content and is also strongly oxidized. Although the amount of data is limited, it appears that the crystallization behavior of present day plantation palm oils is not much affected by differences in origin, provided they are on a comparable level of quality with regard to acidification and oxidation and are obtained predominantly from Tenera breeds.

FRACTIONATION OF PALM OIL

The fractionation process consists of crystallization of that portion of the glycerides that solidify at the temperature of operation followed by their separation from the remaining liquid portion. The latter fraction is generally referred to as olein, and the higher melting portion is called stearin.

Palm oil is fractionated, for instance, to obtain cooking oil, solid fractions for margarine blends, either as such or after randomized or directed interesterification (21), and cocoa butter substitutes (extenders). The latter are predominantly composed of symmetric mono-oleo-disaturated triglycerides and can be used as such or blended with cocoa butter.

Fractionation Methods

Because of the widespread possibilities of application of palm oil fractions, a series of quite different processes was elaborated. The large number of currently published patents illustrates the inherent difficulty of producing sharply defined fractions, i.e., crystals of a size suitable for easy filtration or static or dynamic settling with minimum occlusion of liquid oil, corresponding to the required temperature ranges.

These fractionation processes can be subdivided into

TABLE VI
Effect of Origin on Crystallization Behavior

Number	Origin ^a	% FFA (mol wt 256)	Absorbance ^b		Carotene (ppm)	Tocopherol ^c (ppm)	Peroxide value (meq/kg)	Anisidine value	Iron (ppm)	SPB bleach (5¼ in. cell)
			233 nm	269 nm						
V1	Malaysia	1.41	1.209	0.161	627	617	0.60	2.73	3.46	1.0 red
V2	Malaysia	3.69	1.269	0.228	602	1007	0.32	4.50	5.63	3.2 red
V6	Sumatra	2.17	1.483	0.250	569	803	1.80	3.82	4.90	1.8 red
V11	Cameroon	2.37	1.300	0.243	1154	1121	0.10	3.79	3.85	2.5 red
V71	Zaire	1.98	1.948	0.205	557	879	1.53	4.84	4.26	1.7 red
V91	Zaire	4.26	2.707	0.573	568	705	1.76	9.72	7.92	brownish
V131	Dahomey	5.26	2.170	0.564	1178	1163	1.12	7.95	16.55	brown

Solid fat content by pulsed nuclear magnetic resonance (%)								
		10 C	15 C	20 C	25 C	30 C	35 C	40 C
V1	Malaysia	65.2	45.8	34.1	21.3	11.2	5.7	0.2
V2	Malaysia	64.6	45.7	33.5	20.7	11.6	5.6	0.6
V6	Sumatra	65.6	45.5	33.7	21.7	12.5	6.2	2.5
V11	Cameroon	65.5	43.8	31.8	18.0	8.1	3.3	0
V71	Zaire ^d	65.1	(41.5)	31.0	19.4	10.7	5.6	0
V91	Zaire ^d	54.8	(38.5)	27.5	16.7	8.7	3.5	0
V131	Dahomey	54.0	37.5	27.8	16.7	9.6	3.9	1.3

^aAll samples, except V131, were taken at the production centers. V131 was sampled as loaded into overseas ship tanks.

^bCorrected for carotene.

^cDiphenyl picryl hydrazyl (DPPH) method.

^dComputed from wide-line nuclear magnetic resonance figures.

TABLE VII
Fractionation Methods Applied to Palm Oil on an Industrial Scale

Dry fractionation		Wet fractionation		Fractionation with aqueous detergent	
Major fraction	Olein	Major fraction	Olein	Major fraction	Olein
Cooling to 28 C - 30 C followed by static settling	60%	CMB process (23) in hexane Two crystallizations Iodine value = 60	75%	Lipofrac process (27)	80%
Cooling to 18 C followed by filtration on continuous belt (22)	60%	HLS process ^a (24) in isopropanol HLS process with interesterification Iodine value = 80 (25)	60% 65%		
Fractionation without or with directed or random interesterification to produce components for margarine blends (21)		Cocoa butter substitute intermediate crystallization fraction, yield 30% in acetone (26)			

^aPilot plant scale.

- Fractionation without solvents, or "dry fractionation"
- Fractionation with solvent, or "wet fractionation"
- Fractionation in the presence of an aqueous detergent.

Table VII illustrates the most recent applications of these processes, some of which have already been used for over 20 years. This table also includes a pilot plant scale wet fractionation process, coupled to interesterification. While it is not possible to produce "salad oil" with acceptable yields from palm oil just by fractionation of the triglycerides, this example illustrates further possibilities.

This list does not attempt to be complete, but we have had the opportunity to examine samples of fractions obtained in industrial plants using each process (Table VIII).

Dry Fractionation

Polymorphism and mainly the high viscosity of palm oil at low temperatures do not allow sharp separation of the phases, and consequently the cold test temperature for the

olein fraction is rather high. This type of process avoids the risks of contamination and can be carried out with minimum handling and heating, with beneficial results with regard to oxidation, provided the natural antioxidants are not removed before transport and storage. This happened, in fact, to sample A, bleached before shipping. Sample B has very low oxidation values as compared to all the other samples.

Wet Fractionation

Solvent crystallization produces stable crystal forms. This process offers the highest versatility for any "tailor made" fraction. It is the only one allowing the separation of the intermediate fraction used as cocoa butter substitute.

Numerous recent patents are mainly concerned with the improvement of technology, e.g., other types of solvents, such as acetone/isopropanol mixtures (29), freon (30), methyl ethyl ketone (31), addition of filter aids (32), and crystal modifiers (33).

Great care must be taken to avoid oxidation both of the liquid and solid fractions by contamination from impurities

TABLE VIII
Characteristics of Palm Oil Fractions from Industrial Fractionation Processes (Table VII)

	Process											
	Dry fractionation				Wet fractionation in hexane (CMB, Ref. 23)				Fractionation with aqueous detergent (Lipofrac, Ref. 27)			
	Ivory Coast		Malaysia		Malaysia		Malaysia		Malaysia		Malaysia	
	A		B		C		E		F		D	
	Olein	Stearin	Olein	Olein	Olein	Olein	Olein	Olein	Olein	Olein	Olein	Stearin
FFA (mol wt 256) (%)	<0.1	<0.1	0.17	0.17	2.84	4.95	2.92	3.37	2.01			
Carotene (ppm)	-	-	647	647	476	593	379	503	125			
Tocopherol (ppm) ^b	-	-	761	761	509	996	647	887	308			
Absorbance												
233 nm ^c	-	-	2.263	2.263	1.823	2.469	2.184	2.290	1.491			
269 nm ^c	-	-	0.217	0.217	0.886	0.223	0.240	0.800	0.683			
Peroxide value (meq/kg)	19.2	18.0	12.4	12.4	3.18	3.2	8.1	0.64	0.64			
Anisidine value	19.5	18.4	4.85	4.85	12.7	6.3	3.4	21.1	8.93			
Iron (ppm)	-	-	0.6	0.6	4.1	4.3	16.1	4.4	21.0			
Copper (ppm)	-	-	<0.05	<0.05	0.06	<0.05	0.06	0.06	0.07			
SPB bleach (5% in. cell)	-	-	2.2 red	2.2 red	-	-	-	3.8 red	brown			
strong rancidity			heat bleach only	heat bleach only								
Iodine value (Hanus)	58.2	43.0	58.4	58.4	59.6	57.4	39.3	59.6	27.1			
Fatty acid composition (%)												
C12:0	-	-	0.1	0.1	0.1	0.2	0.1	0.1	0.1			2.1
C14:0	-	-	1.5	1.5	0.5	1.4	0.6	1.6	1.4			0.6
C16:0	-	-	41.5	41.5	35.4	36.1	50.2	32.7	64.1			14.5
C18:0	-	-	5.31	5.31	4.9	4.9	5.7	6.0	5.7			8.2
C18:1	-	-	40.2	40.2	44.6	44.9	33.3	44.7	23.5			1.0
C18:2	-	-	10.8	10.8	14.0	12.3	10.1	14.6	5.0			3.6
C20:0	-	-	0.3	0.3	0.2	0.1	-	0.15	29.2			4.1
C18:3	-	-	0.2	0.2	0.2	0.1	-	0.1	-			-
Cold test (C)	20	-	20	20	18	17	-	18	-			-
Slip point (C)	-	45.6	22.8	22.8	22.5	23.3	50.1	22.2	53.6			-
Solid fat content (%) (pulsed NMR)												
10 C	-	-	36.6	36.6	1.0	0	61.7	0.2	86.3			98.8
15 C	-	-	26.2	26.2	0	0	57.4	0	75.9			92.1
20 C	38.4 ^d	-	13.9	13.9	0	0	49.4	0	70.1			89.9
25 C	4.3	-	0	0			39.2		60.7			86.3
30 C	0.5	-					30.3		53.2			82.1
35 C		-					23.8		40.4			66.6
40 C		-					15.6					
45 C		-					10.2					
50 C		-					0					
55 C		-					0					
60 C		-					0					0.6

^aTiriaux (22).

^bDiphenyl picryl hydrazyl (DPPH) method.

^cCorrected for carotene content.

^dValues computed from dilatometric data, according to Van Putte (28).

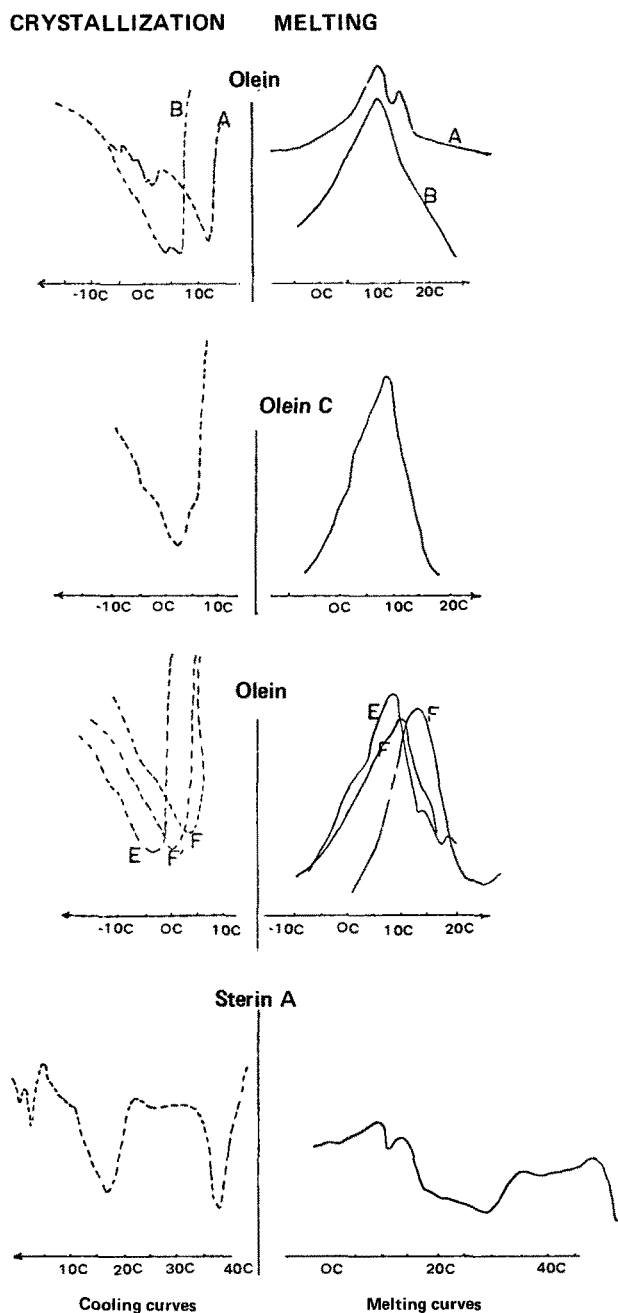


FIG. 3. Differential scanning calorimetry of fractionated palm oil samples.

in the solvent and during stripping. The processes listed in Table VII all operate on the industrial scale, except the HLS fractionation. The latter allows static separation of the solid phase because it crystallizes with a certain amount of solvent which produces crystals of lower density than the miscella.

Fractionation with Aqueous Detergents

The Lipofrac process is a modern version of the "Lanza" process which was used in Nigeria over 20 years ago. After crystallization, aqueous detergent (Na alkyl sulfate) is added, which improves the separation of the liquid oil from the crystals. The fractions are separated by centrifuging and then dried. After normal refining, the residual detergent content drops below 0.1 ppm. Other surface active agents, such as dioctylsulfosuccinate or sodium soap, are used as an alternative and give approximately similar results.

Fractionation of Palm Oil in Practice

Fractionation plants are currently being set up, not only in combination with refineries in consumers' countries but also in palm oil producing countries. Malaysia, at present, produces fractionated palm oil in a number of factories, using all three types of processes.

Quality of Fractionated Palm Oil

Table VIII and Figure 3 show the characteristics of some industrially produced palm oil fractions. A number of chemical characteristics were measured to allow comparison with the quality of normal unprocessed palm oil.

If we consider more specially the olein fractions (not including sample D), it appears that none of the samples remains completely clear at room temperature. The cold tests (maximum temperature of crystal formation after 16 hr storage) vary between 17 C and 20 C; this is unsatisfactory for table oils in countries with a temperate climate.

For frying oil, common practice requires a solid fat content below 5% at 20 C (J. Lefèbvre, Harburger Ölwerke, Hamburg, private communication), and these exigencies are not met by the samples from dry fractionation. In the present series, the lowest solid content was shown by the fractionation with aqueous detergent (DSC curves and cold test of olein E), and the hexane fraction C produced the strongest oxidation for reasons already outlined above (see anisidine value and UV absorbancies).

The efficiency of fractionation is also reflected in the fatty acid composition of the stearin phase. Whenever the solid fraction contains only a low amount of unsaturated fatty acids, the amount of intermediate phase increases in the olein fraction with ensuing increase of the tendency to settle out solids (e.g., difference in DSC curves and cold test between the stearin fractions E and F).

Variations both for fractionation and degree of oxidation appear also within one type of process and even amongst samples from the same plant, as can be seen from samples F and F' from the same plant. The shift in DSC curves is quite pronounced here; the fatty acid composition is also different.

These examples illustrate the difficulty of correct monitoring of the fractionation process. The samples were taken at random, and certainly better results can be obtained both for fractionation and limitation of the degree of oxidation. It stresses the importance of careful quality control both for oxidation and crystallization behavior.

Influence of Transport on Olein Fraction

Until now, only a limited amount of olein fraction from palm oil has been analyzed before and after overseas shipping from Malaysia.

If crude palm oil is fractionated before transport, the risk of oxidation of the olein fraction is evidently higher than for normal unprocessed crude palm oil because of supplementary handling per se. This is shown by the increase of oxidation values during transport, which is slightly higher for the olein fraction tested than for normal crude palm oil (Table IX). However, this oxidation seems relatively small because the olein is completely melted at 30 C and thus necessitates little heating during storage and transport.

When olein or stearin are bleached before transport, they are much more liable to oxidative deterioration, as shown by sample A in Table VIII. This was also found for unfractionated palm oil in previous tests.

A further risk to deterioration is possible contamination by unfractionated palm oil during transport, since few bulking installations make allowance for separate handling for processed oils, especially at outturn in Europe.

At present, we have not had much experience with how the stearin fractions stand transport. Examination of their

TABLE IX

Olein Fraction of Palm Oil (Fractionation with Aqueous Detergent):
Influence of Overseas Transport (Singapore to Rotterdam)

	Olein fraction F'		Average Malaysian palm oil	
	Loading	Outturn ^a	Loading	Outturn ^a
FFA (mol wt 256) (%)	3.54	3.59	3.15	3.24
Moisture (%)	0.069	0.114	0.09	0.10
Carotene (ppm)	599	562	991	529
Tocopherol ^b (ppm)	927	562	991	780
Iron (ppm)	-	3.38	3.76	5.24
Copper (ppm)	-	0.05	0.040	0.052
Absorbance ^c				
233 nm	2.240	2.932	1.709	2.609
269 nm	0.317	0.668	0.290	0.431
Peroxide value (meq/kg)	1.97	5.05	4.22	4.82
Anisidine value	8.52	12.73	4.9	6.10
SPB bleaching test	2.6 red	2.6 red	3.2 red	3.2 red
	26 yellow	26 yellow	32 yellow	32 yellow
Iodine value	58.2	58.2		
Fatty acid composition of the olein fraction at loading (%)				
C _{12:0}	0.28		C _{18:0}	3.50
C _{14:0}	1.1		C _{18:1}	43.80
C _{16:0}	37.90		C _{18:2}	13.20
C _{16:1}	0.05		C _{20:0}	0.05
			C _{18:3}	0.09

^aJust after arrival in Europe.

^bDiphenyl picryl hydrazyl (DPPH) method.

^cCorrected for carotene content.

chemical characteristics (Table VIII), however, shows that the oxidation products and heavy metals tend to concentrate in the stearin phase, while the olein phase becomes richer in antioxidants. This should clearly act detrimentally on the stability of the stearin fraction, in spite of its lower unsaturation.

From the preceding, it appears that similar considerations apply to quality criteria for fractionated palm oil as apply to crude palm oil, and this emphasizes particularly the need for systematic quality control in a similar manner to that already undertaken for the production and transport of crude palm oil (18,34).

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