# PALM OIL FRACTIONATION AND CAROTENE EXTRACTION

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by

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# DECLARATION

I, BOEY PENG LIM, do hereby declare that the work described in this thesis was carried out by me in the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. I further declare that this work has neither been accepted nor being concurrently submitted in candidature for any other degree.

Signed: ______________________ Date: 28/4/78

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(PROFESSOR A.S.H. ONG)

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# ABSTRAK

Suatu kaedah pemisahan yang baru bagi minyak sayur, minyak haiwan dan minyak ikan dan terutamanya bagi minyak kelapa sawit akan diperikan dalam tesis ini. Kaedah ini melibatkan penambahan kepada minyak itu suatu bahantara yang terdiri dari dua pelarut yang biasa. Semasa pengemparan, olein dan stearin dipisahkan oleh bahantara yang didapati di antara bahagian pepejal dan cecair. Dua belas sistem pelarut atau bahantara yang terdiri daripada suatu gabungan dua daripada lapan pelarut yang biasa, iaitu air, propilena glikol, gliserin, aseton, etanol, n-propanol, isopropanol dan butanon didapati berkesan dalam pemisahan olein-stearin. Bagaimanapun, sistem air-isopropanol telah dikaji dengan lebih lanjut. Proses pemisahan boleh dilaksanakan pada sebarang suhu yang sesuai dan proses ini tidak bersandar kepada kaedah penghabluran minyak itu. Pemisahan minyak kelapa sawit mentah Special Prime Bleached (SPB atau Minyak Kelapa Sawit yang dilunturkan dengan Khusus) pada suhu 16°C dengan menggunakan sistem air-isopropanol menghasilkan suatu pecahan olein yang mempunyai suatu takat awan sebanyak 4.8°C. Bahantara yang digunakan boleh digunakan semula sehingga tujuh kali. Pemisahan minyak isi kelapa sawit yang berhidrogen menghasilkan suatu pecahan stearin yang mempunyai takat lebur 36°C yang serupa dengan mentega koko. Proses pemisahan ini boleh juga diperluaskan dengan pengubahsuaian yang sesuai termasuk penyah-pelekatan dan peneutralan. Pecahan-pecahan olein yang diperolehi setelah pemisahan didapati tanpa fosfatid dan kandungan asid lemak bebas berkurang serendah 0.02%. Perkembangan pemisahan ini ke dalam suatu proses selanjar telah

ditunjukkan dengan menggunakan Pemisah Alfa-Laval LAPX 202.

Dari kajian pemisahan bagi pelbagai minyak dari kelapa sawit kacukan, Kacukan Antara-Spesifik $F_1$ (E. oleifera x E. guineensis (Pisifera sebagai asas) ) keputusan-keputusan yang diperolehi memberi harapan yang baik. Apabila minyak itu dipisahkan pada suhu 15°C, hasil olein adalah 87.7%, takat awannya adalah 1.7°C dan nilai iodinnya adalah 66.7 dan ketaktepuan jumlah adalah 63% manakala stearin sepadan yang diperolehi itu mempunyai suatu takat lebur sebanyak 49.0°C.

Pemisahan minyak kelapa sawit mentah dengan menggunakan cerun-ketumpatan menghasilkan enam pecahan stearin yang mempunyai ciri-ciri peleburan yang berlainan (47.5°C hingga 55.3°C) dan komposisi asid lemak (ketaktepuan 48.4% hingga 34.9%).

Selain daripada pemisahan, penemuan ini boleh juga dipakai untuk menentukan kandungan olein di dalam minyak kelapa sawit. Suatu pertalian yang baik didapati wujud antara peratusan olein yang ditentukan sedemikian pada suhu 29°C dan komposisi asid lemak.

Suatu campuran yang terdiri dari 80% air dan 20% isopropanol yang mengandungi natrium hidroksida telah didapati boleh meneutralkan minyak kelapa sawit dan minyak isi kelapa sawit tanpa pembentukan bauran, manakala meminimumkan kehilangan minyak sehingga 4.8% . Kehilangan minyak dengan menggunakan natrium hidroksida berair adalah 7.6% .

Suatu kajian mengenai kesan sinergistik lesitin dengan pelbagai anti-oksidan biasa untuk menstabilkan minyak memperlihatkan bahawa kuantiti anti-oksidan yang digunakan boleh dikurangkan dengan lebih banyak lagi. Telah didapati bahawa apabila 0.05% lesitin ditambahkan hanya 1/8 kepekatan asli t-butil hidrokuinon (TBHQ) atau 1/20 kepekatan asli hidroksi anisola berbutil (BHA) atau hidroksi toluena berbutil (BHT) apabila digunakan secara berasingan adalah diperlukan untuk memberi kestabilan-AOM yang sama.

Pembersihan minyak kelapa sawit secara biasa akan memusnahkan karoten yang didapati di dalamnya. Di sini, suatu kaedah untuk mengekstrakkan karoten dengan menggunakan karbon yang diaktifkan yang dihasilkan secara tempatan dihuraikan. Ekstrak karoten yang diperolehi (dengan menggunakan karbon S511) adalah kira-kira enam kali ganda kepekatan karoten yang didapati dalam minyak asli itu. Karoten-karoten yang diekstrakkan adalah aktif secara biologi dan tidak berbahaya kepada haiwan sepertimana yang dipastikan oleh eksperimen-eksperimen memberi makanan yang menggunakan tikus bulai dan suatu kajian histologi mengenai organ-organnya. Kajian penyerapan mengenai karbon-karbon yang diaktifkan memperlihatkan bahawa karbon pH sekitar 10.8 dan mempunyai luas permukaan yang besar serta memiliki bilangan mesopora yang besar adalah sesuai untuk pengekstrakkan karoten.

# ABSTRACT

A novel method of fractionation of vegetable, animal and fish oils and in particular palm oil is described. The method involves the addition to the oils a medium made up of two common solvents. On centrifugation the olein and stearin are separated by the medium in the middle. Twelve solvent systems or media which are made up of a combination of two from eight common solvents viz. water, propylene glycol, glycerine, acetone, ethanol, n-propanol, isopropanol and butanone are found to be effective in olein-stearin separation. However, the water-isopropanol system was studied in great details. The fractionation process can be carried out at any suitable temperature and is independent of the method of crystallisation of the oil. Fractionation of the Special Prime Bleached (SPB) crude palm oil at 16°C using the water-isopropanol system, yielded an olein fraction with a cloud point of 4.8°C. The used medium can be re-used up to seven times. Fractionation of hydrogenated palm kernel oil yielded a stearin fraction similar in melting characteristic (36°C) to that of cocoa butter. This fractionation process could also be extended with suitable modifications to include degumming and neutralisation. The olein fractions obtained after fractionation were found to be free from phosphatides and the free fatty acid content was reduced to as low as 0.02%. The development of this fractionation into a continuous process has been demonstrated using the Alfa-Laval LAPX 202 Separator.

From the fractionation study of the various oil from hybrid palms, the Interspecific Hybrid $F_1$ ( E. oleifera x E. guineensis (Pisifera based) ) was found to be promising. When the oil was fractionated at 15°C, the yield of olein was 87.7%, its cloud point 1.7°C and its iodine value 66.7 and the total unsaturation was 63% whilst the corresponding stearin obtained has a melting point of 49.0°C .

Fractionation of crude palm oil using density gradients yielded six stearin fractions of different melting characteristics (47.5°C to 55.3°C) and fatty acid composition (unsaturation 48.4% to 34.9%).

Besides fractionation, this finding could also be applied to the determination of the olein content of palm oil. A reasonable relationship was found to exist between the percentage of olein thus determined at 29°C and the fatty acid composition.

A mixture of 80% water and 20% *iso*propanol containing sodium hydroxide was found to effect neutralisation of palm oil and palm kernel oil without the formation of emulsion, while minimising oil loss to 4.8% . Oil loss using aqueous sodium hydroxide was 7.6% .

A study on the synergistic effect of lecithin with various common antioxidants in stabilising oils showed that the amount of antioxidants used could be very much reduced. It was found that when 0.05% of lecithin was added only 1/8 of the original concentration of *t*-butyl hydroquinone (TBHQ) or 1/20 of the original concentration of butylated hydroxy anisole (BHA) or butylated hydroxy toluene (BHT) when used singly was required to give the same AOM-stability.

Normal refining of crude palm oil destroys the carotenes present in it. Here, a method of extracting the carotenes with locally produced activated carbons is described. The carotene extract obtained (using S511 carbon) is about six times that of the concentration of carotene in the original oil. The extracted carotenes are biologically active and not toxic to animals as confirmed by feeding experiments using albino rats and a histological study of their organs. The sorption study on the activated carbons shows that carbons of pH around 10.8 with large surface area and possessing large numbers of mesopores are suitable for carotene extraction.

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# PART I

# FRACTIONATION OF PALM OIL

## 1 INTRODUCTION

Oil palm was first brought to Malaysia in 1870 mainly as an ornamental plant. Commercial planting of this crop only began fifty years later. Today Malaysia, the largest exporter of palm oil in the world, produces 48% of the total world production and contributes 71% of all palm oil exports in 1977[1]. The production is expected to reach 2.5 million tons in 1980 as compared to 1974's production of just over one million tons (See TABLE 1.1).

TABLE 1.1

PROJECTED PRODUCTION (1974-1980) OF PALM OIL[1,2,3]

| Year | Production (,000 tons) |
|---|---|
| 1974 | 1047 |
| 1975 | 1254 |
| 1976 | 1455 |
| 1977 | 1650 |
| 1978 | 2050 |
| 1979 | 2362 |
| 1980 | 2670 |

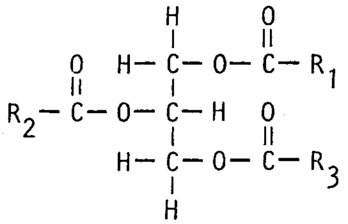
Oil palm is by far the highest yielding oil crop (See TABLE 1.2). Two types of oil can be obtained from the oil palm fruits viz. palm oil and palm kernel oil. Palm oil is extracted from the fibrous layer of pulp on the outside (the mesocarp) of the fruit and palm kernel oil from the kernel.

## TABLE 1.2

## YIELD OF OIL FROM VARIOUS OIL-PRODUCING PLANTS[2]

| Plant | Pounds per acre |
|---|---|
| Malaysian oil palm (mesocarp) | 3300 |
| Malaysian oil palm (kernel) | 370 |
| Coconut | 1120 |
| Peanut | 780 |
| Soybean | 340 |

Palm [illegible]s a li[illegible]lid (st[illegible]) [illegible]ents at [illegible] room temperature (about 29°C) while palm kernel oil is liquid at this temperature. The oils like other vegetable oils, are glyceryl esters of fatty acids, or triglycerides (See FIGURE 1.1).



$R_1$, $R_2$ and $R_3$ are carbon chains of varying chain length and degree of unsaturation

FIGURE 1.1 STRUCTURAL FORMULA OF TRIGLYCERIDE

Palm oil contains many triglycerides which differ in the types of fatty acid present. The fatty acid components present as triglycerides in it are as in TABLE 1.3.

## TABLE 1.3

## FATTY ACIDS PRESENT AS TRIGLYCERIDES IN MALAYSIAN PALM OIL[4,5]

| Carbon atom | Chemical name | Common name | % of total acids |
|---|---|---|---|
| $C_{14}$ | Tetradecanoic | Myristic acid | 0.5 |
| $C_{16}$ | Hexadecanoic | Palmitic | 48.3 |
| $C_{18}$ | Octadecanoic | Stearic | 2.9 |
| $C_{18:1}$ | 9-Octadecenoic | Oleic | 40.0 |
| $C_{18:2}$ | 9,12-Octadecadienoic | Linoleic | 8.3 |

Other fatty acids such as lauric (Dodecanoic), palmitoleic (9-hexadecenoic), arachidic (Eicosanoic) and linolenic (9,12,15-octadecatrienoic) are also present in trace amounts. The triglyceride composition of Malaysian palm oil is shown in TABLE 1.4.

## TABLE 1.4

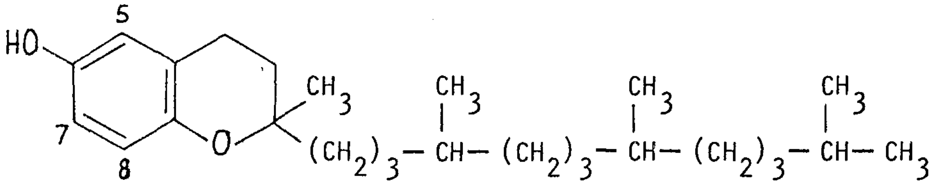
## TRIGLYCERIDE COMPOSITION OF MALAYSIAN PALM OIL[4,6]

| Glyceride type | Component | Composition (%) |
|---|---|---|
| Trisaturated | SSS | 8.0 |
| Disaturated | 2-oleodisaturated (SOS) | 35.5 |
|  | 1-oleodisaturated (OSS) | 3.0 |
|  | 2-Linoleodisaturated (SLS) | 8.0 |
| Monosaturated | Dioleo monosaturated (SOO + OSO) | 29.0 |
|  | Linoleo monosaturated (SOL) | 9.0 |
| Triunsaturated | UUU | 7.5 |

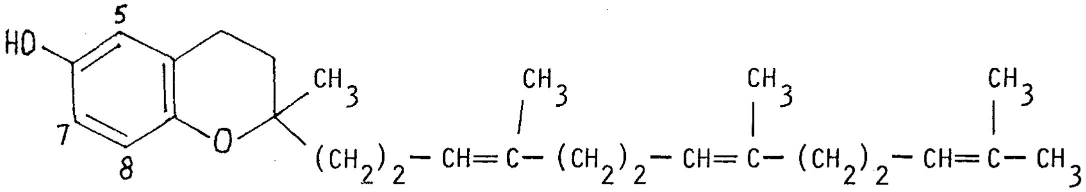
Monoglycerides and diglycerides contain one and two fatty acids respectively, and consequently have two and one free hydroxyl groups. They do not occur naturally in appreciable quantities except in oils that have undergone partial hydrolysis.

Small amounts of non-glyceridic components are also present in palm oil, such as phosphatides, alcohols, sterols, tocopherols and carotenoids. Phosphatides are present in about 500 ppm[4,7]; triterpenic and aliphatic alcohol in about 800 ppm[4,7]. The sterol content in palm oil is relatively low (<300 ppm)[7,8,9], the major sterols present being β-sitosterol (63% of total sterols), campesterol (21%) and stigmasterol (12%). Cholesterol constitutes approximately 4% of the total sterols present in palm oil[5]. Malaysian palm oil contains 500-800 ppm[4,7] tocopherols, which are known for their vitamin E activity. They also have antioxidant effect on palm oil. Since the word tocopherols in most texts is taken to mean a mixture of both tocopherols and tocotrienols, the author follows the same usage of the word unless distinction is made to mean either tocopherol or tocotrienol. The naturally occurring forms are eight in number and could be classified under the tocol series and the tocotrienol series (See FIGURE 1.2).

The tocopherols present in palm oil have been reported as shown in TABLE 1.5.



Tocol



Tocotrienol

| Position of methyl group | Tocopherol | Tocotrienol |
|---|---|---|
| 5,7,8 Trimethyl | α | α |
| 5,8 Dimethyl | β | β |
| 7,8 Dimethyl | γ | γ |
| 8 Monomethyl | δ | δ |

FIGURE 1.2 STRUCTURES OF TOCOPHEROLS AND TOCOTRIENOLS

## TABLE 1.5

## TOCOPHEROLS IN MALAYSIAN PALM OIL[10,11]

| Tocopherol | Composition (%) | Vitamin E activity*(iu/mg) |
|---|---|---|
| $\alpha$ | 35 | 1.10 — 1.49 |
| $\gamma$ | 35 | 0.15 — 0.20 |
| $\delta$ | 10 | 0.012 — 0.016 |
| tocotrienol | 20 | — |

* 1 iu of vitamin E corresponds to the activity of 1 mg of synthetic racemic vitamin E acetate.

However, recent investigations[12] into the tocopherol composition of palm oil revealed that tocotrienols are the major tocopherols present. They represent over 70% of the total tocopherols in palm oil. The results obtained by two dimensional thin layer chromatography followed by colorimetric determination of the individual tocopherols are shown in TABLE 1.6.

## TABLE 1.6

## TOCOPHEROL AND TOCOTRIENOL CONTENT OF CRUDE PALM OIL

| | Composition+(%) | |
|---|---|---|
| | Tocopherol | Tocotrienol |
| $\alpha$ | 28.3 | 19.5 |
| $\beta$ | - | 3.9 |
| $\gamma$ | - | 40.0 |
| $\delta$ | - | 9.4 |
| Total | 28.3 | 72.8 |

+ The data given are average of four duplicate samples.

Analysis by gas-liquid chromatography using glass capillary column packed with OV-17 also revealed that the major tocopherols present in palm oil are tocotrienols[13]. TABLE 1.7 shows the results of a typical analysis.

TABLE 1.7

TOCOPHEROL CONTENT OF PALM OIL

| | Composition (%) | |
|---|---|---|
| | Tocopherol | Tocotrienol |
| α | 21.5 | 7.3 |
| β | 3.7 | 7.3 |
| γ | 3.2 | 43.7 |
| δ | 1.6 | 11.7 |
| Total | 30.0 | 70.0 |

The tocopherols present in palm oil not only protect the oil from oxidation but also serve as a source of vitamin E. Phosphatides, another trace component of palm oil, play an important role in blood coagulation[14]. They are essential for the formation of blood thromboplastin of which they constitute a structural component.

Autoxidative rancidity of fats is the result of autoxidation of fatty acids. Polyunsaturated acids oxidise more rapidly than mono-unsaturated acids. Exposure of polyunsaturated oils during deep frying can result in formation of oxy-polymers which are hazardous to health. Many workers[15-17] had observed that feeding linseed oil previously heated at 275°C to rats resulted in paralysis, decrease in body weight gain and higher death rate. It was suggested that the primary cause was due to toxicity of the cyclized or branched chain acids formed in the course of oxidation. Malaysian palm oil with only 8-10% linoleic acid is therefore less prone to oxidation. Thus the formation of oxidised products during deep frying is low as compared to other more unsaturated oils (See FIGURE 1.3).

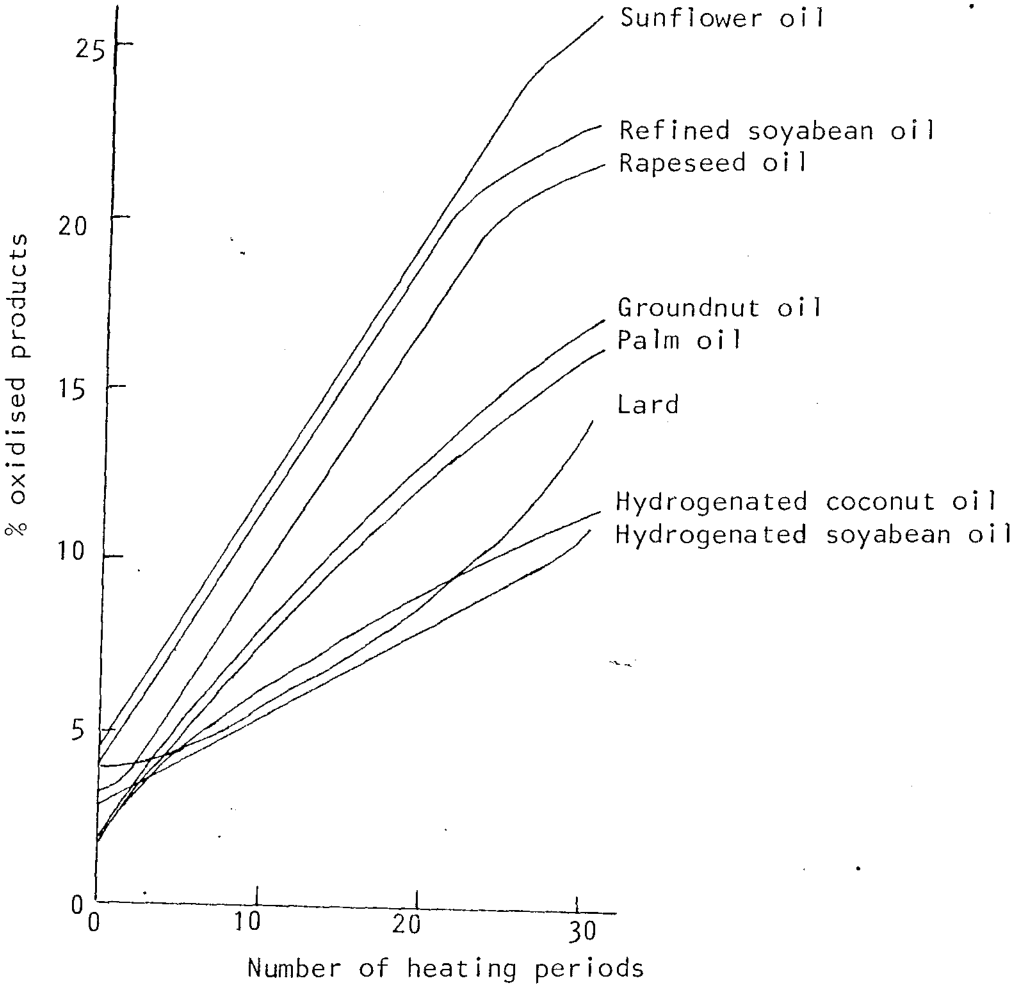


FIGURE 1.3 <u>OXIDATION OF OILS AND FATS DURING DEEP FRYING</u>[4]

Palm oil on the world market, faces stiff competition from other edible oils and fats. In order to compete effectively, efforts towards improving the quality and finding more end-use applications are of prime importance. It is a combination of quality, end-use applications, reliable supply and fair market prices that help win more users of Malaysian palm oil. Definite steps have been taken to obtain high quality palm oil as well as finding more end-uses of the oil. On the planting material, extensive breeding programmes[18-28] are launched in obtaining oil palms producing oils containing a higher proportion of unsaturated acids. Some preliminary work has been done on the oils from the various hybrid palms[29,30]. The cross known as Interspecific Hybrid $F_1$ (E. guineensis X E. oleifera) is promising. There is an increase in unsaturated fatty acids and its oil composition is intermediate between that of E. oleifera and E. guineensis.

One way of extending the end-uses of palm oil is through fractionation which normally yields olein (liquid) and stearin (solid) fractions. This subject of fractionation has been reviewed by many workers[31-34]. The various methods used in the fractionation of palm oil are:

1) Winterisation
2) the Tirtiaux Process
3) the Detergent Process
4) Crystallisation with isopropanol which contains about 5% water.
5) Crystallisation with organic solvents such as hexane, acetone, nitropropane and propane.

Fractionation by winterisation involves crystallisation prior to the separation of the liquid and solid fractions. The separation can be achieved by decantation, but this represents a great loss of the liquid fraction which is of higher commercial value, as considerable amounts are entrained in the solid fraction. A more practical way is by vacuum filtration. The Tirtiaux Fractionation Process[35] employs a continuous vacuum filter called the Florentine which is equipped with a stainless steel perforated belt. The principle of the process involves three operations, viz. seeding, crystallisation and filtration. The trisaturated triglycerides (m.p.>63°C, about 8% in palm oil) act as seeds. The first operation is to crystallise the trisaturated triglycerides by leaving the oil for at least twelve hours at 45-50°C under slow agitation. The seeded palm oil is then pumped into a crystalliser where crystallisation is carried out by controlled cooling and agitation. The crystallised oil is then fractionated (without using solvents) by continuous vacuum filtration. The De Smet Fractionation Process[36,37] is similar to the Tirtiaux Process. However, hexane and acetone are sometimes used to reduce the viscosity of the oil for speedier filtration. The addition of fatty acid esters of glucose or a glucose derivative such as gluconic acid has been reported[38] to yield easily filterable crystals in the fractionation of fats.

The Detergent Process or the Alfa-Laval Lipofrac Process[39,40] is basically a winterisation process except that a surface active agent is used during centrifugal fractionation. The crystallised oil is premixed with an aqueous solution containing sodium lauryl sulphate and an electrolyte (magnesium sulphate or sodium sulphate). Due to the action of this surface active agent the crystals are wetted by and dispersed in the aqueous phase, their surface being at the same time washed free from the liquid component. The oil phase can be separated from the crystals and the detergent solution by centrifugation. The crystals in the detergent solution is heated until the solid becomes liquid which is then further separated from the detergent solution by centrifugation. Other surface active agents have also been used in a number of fractionation processes[41-45]. Their working principle is similar to the Alfa-Laval Lipofrac Process. The separation of the oil phase from the crystals and the detergent solution can also be achieved by gravity or the oil phase and detergent solution can be separated from the crystals by filtration.

The H.L.S. Process[46,47] developed by Koslowsky is based on crystallisation of palm oil in isopropanol containing water (4-6%). The crystallised solid fraction separates and suspends in the isopropanol phase. The density of the crystals is lower than the density of the liquid phase, hence a rapid separation into two layers occurs. The solid phase can then be separated by decantation without the need for filtration. In a typical example, using one part palm oil to one part solvent system and with fractional crystallisation at 15°C, the upper layer contains about 17% solid fat and 83% isopropanol. The lower layer contains about 84% oil and 16% isopropanol. It has been reported[48] that crystallisation of palm oil in an isopropanol-acetone system (3:1 v/v) produces a fraction suitable for use as cocoa butter.

The C.M.B. (Costruzioni Meccaniche Bernardini) Fractionation Process[49] involves continuous crystallisation of the oil in hexane (1:1 v/v) followed by separation of the liquid and the solid fractions through continuous drum-type filters, and distillation of the two fractions to free them of solvent. If an oil of lower cloud point is required, the filtrate from the first stage crystallisation is further cooled and filtered in a second stage crystallisation at a much lower temperature.

Other fractionation processes[50-52] based on the crystallisation of palm oil in hexane have been reported.

Acetone has also been widely used as a medium for crystallisation to obtain highly unsaturated fractions and cocoa butter substitutes[53-56]. Martinenghi[57] has reported a progressive fractionating process using acetone and hexane.

Crystallisation of palm oil in 1-nitropropane, 2-nitropropane or a mixture of them yields solid fraction suitable as cocoa butter substitutes[58-60]. Fractionation of oils by selective extraction of the triglycerides using liquid propane has been reported[61].

Fractionation of palm oil can also be achieved by transesterification[62]. In this process, the fatty acid radicals in the glyceride molecules and the added saturated fatty acid derivative are transesterified. This results in rearrangement of the fatty acid radicals between the glyceride molecules to yield a liquid fraction rich in triunsaturated glycerides and a solid fraction of mostly trisaturated glycerides.

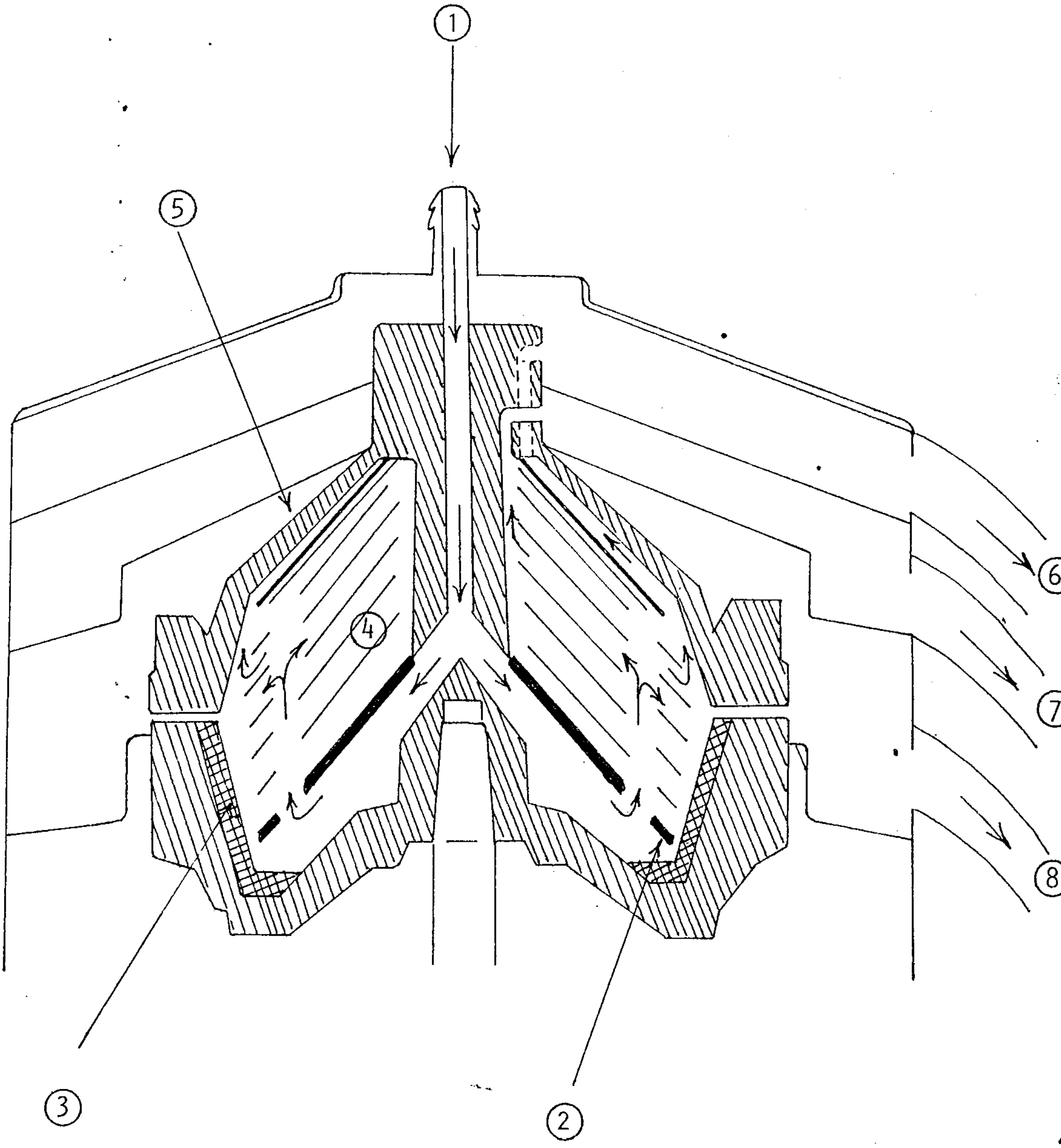
The full conversion of palm oil into unsaturated liquid oil is achieved[63] by the creation of double bonds in the chain of the palmitic acid, which is present in about 48% of the total acids in palm oil. The steps involved include isolation of the saturated palmitic acid (as ethyl palmitate) and chlorination by elemental chlorine using activated carbon as a catalyst. The chlorinated ethyl palmitate is dehydrochlorinated and the newly formed unsaturated $C_{16}$ ester is reintroduced into the oil by transesterification.

All the above mentioned processes have certain disadvantages. In the winterisation process, oil is lost through occlusion in the stearin fraction. In those processes which use organic solvents, there is a danger of inflammability and the high cost of recovering the solvents. In the Detergent Process, trace detergent left in the fractionated products may be hazardous to health and as a result this process is still not acceptable in certain countries. Although the full conversion of palm oil into liquid oil by creating double bonds in the saturated fatty acid is promising, a detailed study of this chemically modified oil is necessary to ensure safety in long term consumption. In view of these disadvantages, it is proposed that the problem of fractionation of palm oil into all its possible components be studied. Efforts are concentrated on finding a new method of fractionation which will overcome some of these disadvantages.

In this thesis, the development of a new fractionation process and the evaluation of the products obtained are described. The development of this fractionation process to a continuous scale involves the use of a centrifugal separator, the Alfa-Laval LAPX-202.

Although there are many types of separators constructed for the particular requirements of a process, their working principle is essentially the same. The principle of centrifugation depends on the centrifugal force which acts on all particles proportionally to their mass, i.e. centrifugal force = $mw^2r$, where m is the mass of the particle, w is the angular velocity of the rotor and r is the distance of the particle from the centre of rotation. The greater the difference in mass, the easier is the separation. However, the size and shape of the particles and the viscosity of the process liquid also play an important part. Large, smooth and round particles are easier to separate than small and irregular ones. Low viscosity improves the separation result.

The Alfa-Laval LAPX 202 Separator is of the disc-type (See FIGURE 1.4). The separator bowl can be opened or closed by the seal ring, which is operated hydraulically. The process liquid is fed in through a stationary feed pipe which opens into the rotating bowl. The distributor directs the incoming liquid mixture into the interspaces of the disc assembly. Through the action of centrifugal force, the liquid phases are separated from each other. The light liquid phase moves along the upper side of bowl discs towards the bowl centre and discharges through holes in the neck of the bowl hood. The heavy liquid phase takes the outward path and proceeds along the top disc towards the neck of the bowl and discharges through holes at the top of the bowl. The solid particles move along the underside of the discs towards the bowl periphery, where they settle on the bowl wall. When the hydraulic pressure is released, the seal ring is forced down by centrifugal force and thus opens the bowl. The solid component is then ejected.



① Process liquid, inlet
② Distributor
③ Seal ring
④ Disc assembly

⑤ Bowl hood
⑥ Heavy liquid phase, outlet
⑦ Light liquid phase, outlet
⑧ Solid phase, outlet

FIGURE 1.4 A DISC-TYPE SEPARATOR BOWL

In almost all palm oil fractionation processes, recrystallisation is necessary in order to effect separation. Different types of crystals suit different processes but in general, large granular type crystals are easier to separate. Crystallisation of palm oil is a very intricate process as the triglycerides exhibit polymorphism i.e. they can exist in different crystal forms of varying degrees of stability. This is due to the stereochemical configuration of the molecules in the crystal which assumes an unsymmetrical "tuning fork" pattern[64,65] with different orientations of the zigzag arrangement of the glyceridic chain. Luton[66] designated $\alpha$, $\beta'$ and $\beta$, in order of stability for the description of polymorphism of glycerides. Those crystals of intermediate stability are distinguished by subscripts, eg. $\beta_1$, $\beta_2$, and they are numbered in the order of decreasing melting points[67].

The different crystal forms, which have been identified by X-ray diffraction have a configuration which is measured by parameters called "short spacing" (See TABLE 1.8) and "long spacing". The "long spacing" is a function of both the chain length of the fatty acids and the angle of tilt between a hydrocarbon chain and the boundary plane of the molecular layer (See FIGURE 1.5).

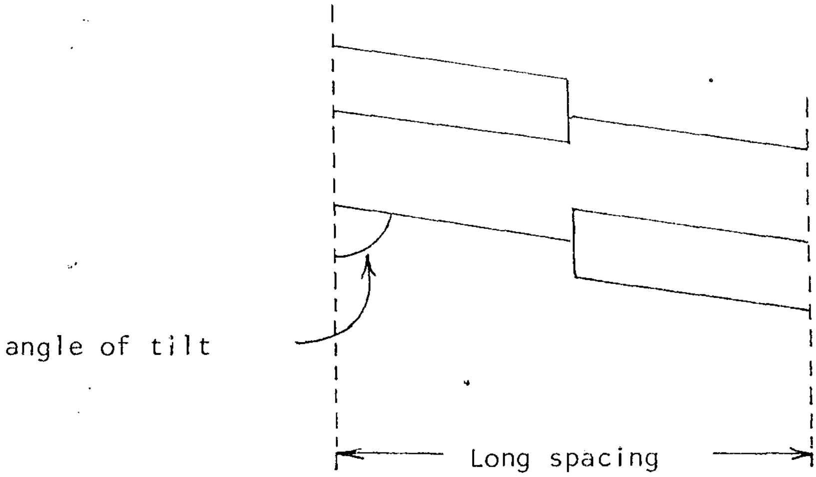


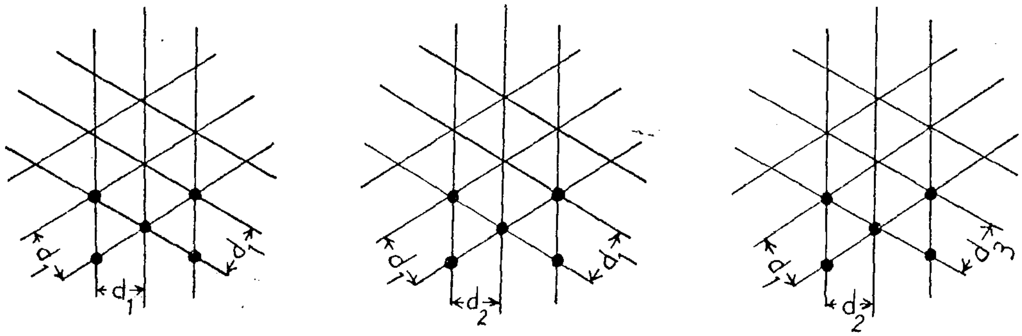
FIGURE 1.5 A POLYMORPHIC STRUCTURE SHOWING THE ANGLE OF TILT AND LONG SPACING

TABLE 1.8

BASIS OF NOMENCLATURE FOR GLYCERIDE FORMS[66,67]

| Form | Short Spacing Pattern Characteristics |
|---|---|
| α | One single strong line near 4.15Å |
| β' | Two strong lines near 4.20Å and 3.80Å or three strong lines near 4.27, 3.97 and 3.71Å. |
| β | One strong line near 4.60Å |

Like all other long chain paraffinic compounds, the zigzag triglyceride chains crystallise with long axes parallel to each other. The cross-sectional arrangements give the primary basis for nomenclature of the various polymorphic forms[66] (See FIGURE 1.6).



α : $d_1$ = 4.14Å

β' : $d_1$ = 4.18Å
$d_2$ = 3.78Å

β : $d_1$ = 3.68Å
$d_2$ = 4.59Å
$d_3$ = 3.86Å

FIGURE 1.6 CROSS-SECTIONAL STRUCTURES OF DIFFERENT POLYMORPHIC FORMS

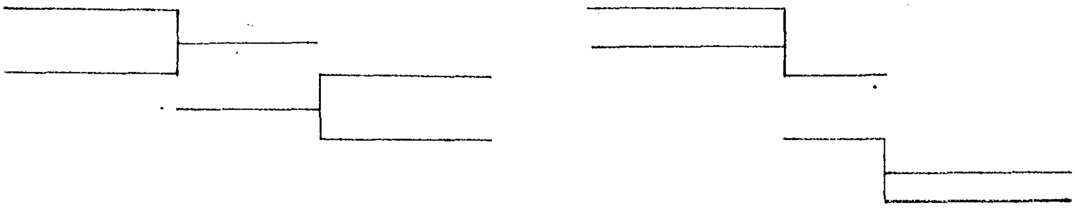
In FIGURE 1.6, the black dots represent the chain axes. The main short spacings to which the arrangements give rise are indicated in the drawing. The α-form can be visualised by grasping tightly a number of rods of equal diameter. This form is a low density structure whose cross-section is about $20\text{Å}^2$ per chain. The β'-form is generally associated with tilted chains, but perpendicular β'-like structures are observed for some long chain compounds[66]. The β-form which is the most stable form is almost invariably associated with tilted chains. Both β' and β forms are more dense in cross-section than α, each chain cross-section occupying about $18.5\text{Å}^2$.

Different arrangements are possible for the triglyceride molecules in the crystal. The most common are the double chain (See FIGURE 1.7) and the triple chain structures[64,68] (See FIGURE 1.8).

Simple triglyceride

Mixed triglyceride

FIGURE 1.7 DOUBLE CHAIN STRUCTURES



"tuning fork" arrangement

"chair" arrangement

FIGURE 1.8 TRIPLE CHAIN STRUCTURES

Fast cooling of melted glycerides, except for short chain triglycerides, produces $\alpha$ and $\beta'_2$ crystals which upon heating passes through the following steps[69]:

$$\beta'_2 \longrightarrow \alpha \longrightarrow \beta' \longrightarrow \beta$$

Palm oil cooled rapidly and then warmed at a rate of 0.5°C per minute was reported to give $\beta'$ crystal[70]. (See FIGURE 1.9).

Rapidly cooled crystals at -10°C

$\downarrow$ -10°C to -5°C

$\beta'_2$ phase

$\downarrow$ -5°C to 7°C

$\alpha$ and $\beta'_1$ phases

$\downarrow$ above 7°C

mainly pure $\beta'_1$ phase

FIGURE 1.9 POLYMORPHIC TRANSFORMATIONS OBSERVED IN PALM OIL

## 2 RESULTS AND DISCUSSION

It is known that density gradients have been used in the fractionation of biochemical specimens by centrifugation[71]. The gradients consist mainly of aqueous sucrose solution or an inorganic salt eg. cesium chloride. However, both these systems have been found to be unsuitable for palm oil. As a result, many density gradients were tried. Those density gradients found to be stable are made up of a combination from eight common solvents viz. water, propylene glycol, glycerine, acetone, ethanol, n-propanol, isopropanol and butanone. There are twelve solvent systems which have been found to be effective[72]. The first density gradient was prepared from glycerine and isopropanol. When crude palm oil was added followed by centrifugation, it was observed that the olein appeared in one layer (20% glycerine, 80% isopropanol) and the stearin in another (30% glycerine, 70% isopropanol). See FIGURE 2.1 .

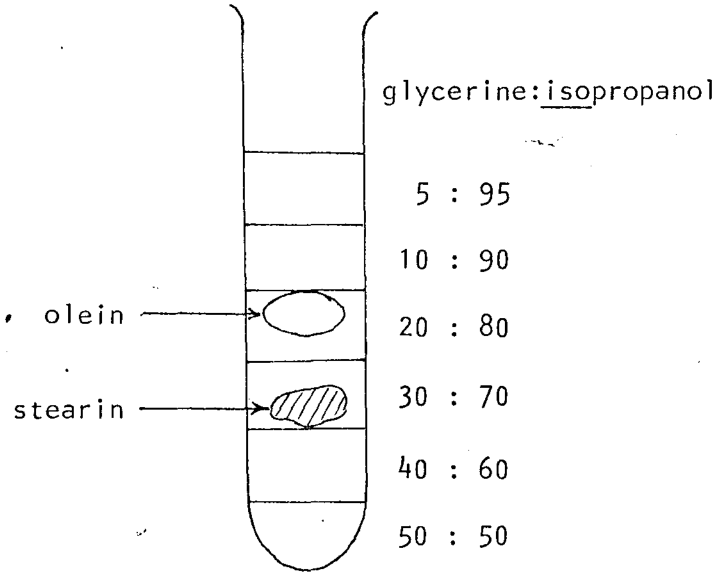


FIGURE 2.1 FRACTIONATION USING DENSITY GRADIENT

From the above observation, it was thought that instead of centrifuging the palm oil with a density gradient, one could choose a medium of the right density which is intermediate between the densities of the olein and stearin to achieve the same results (see FIGURE 2.2) . A preliminary investigation[72] using all the twelve solvent systems was carried out with crude palm oil and the results show that good separation could be achieved over a small range of densities of the medium used (see TABLE 2.1). The composition of the liquid mixture which forms the medium can be defined by the following equation:

$$XD_1 + (100 - X)\ D_2 = B$$

where X is the percentage of component I, $D_1$ is the specific gravity of component I at 25°C, $D_2$ is the specific gravity of component II at 25°C and B depends on the specific gravity of the olein and stearin and varies between 87 - 97.

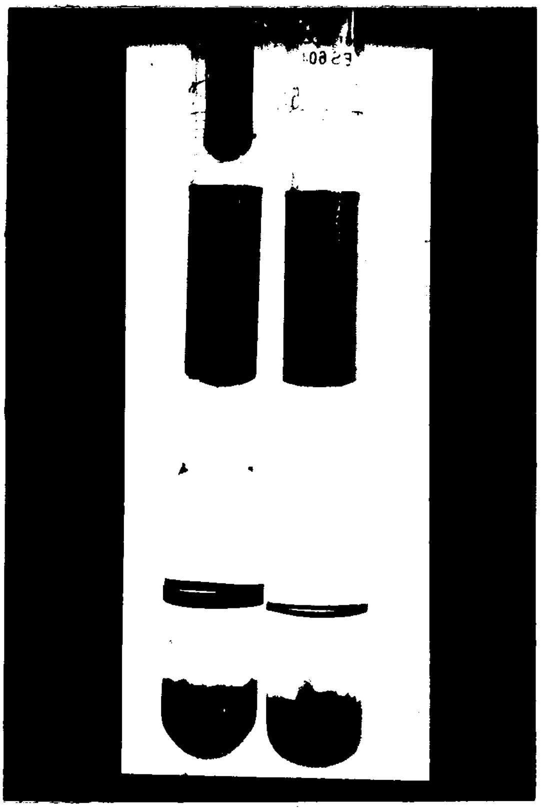


FIGURE 2.2 OLEIN-STEARIN SEPARATION

## TABLE 2.1

## FRACTIONATION OF CRUDE PALM OIL BY CENTRIFUGATION USING THE TWELVE SOLVENT SYSTEMS

| Solvent system | Percentage of Component I | | | |
|---|---|---|---|---|
| I : II | No separation (oil sinks) | Good separation | Partial separation (stearin in olein) | No separation (oil floats) |
| water : acetone | 31 | 32 - 37 | 38 - 52 | 53 |
| water : ethanol | 41 | 42 - 44 | 45 - 58 | 59 |
| water : n-propanol | 42 | 43 - 45 | 46 - 64 | 65 |
| water : isopropanol | 41 | 42 - 45 | 46 - 57 | 58 |
| propylene glycol : acetone | 34 | 35 - 38 | 39 - 62 | 63 |
| propylene glycol : butanone | 24 | 25 - 31 | 32 - 61 | 62 |
| propylene glycol : ethanol | 45 | 46 - 49 | 50 - 64 | 65 |
| propylene glycol : n-propanol | 42 | 44 - 45 | 46 - 65 | 66 |
| propylene glycol : isopropanol | 45 | 47 - 48 | 49 - 66 | 67 |
| glycerine : ethanol | 23 | 24 - 25 | 26 - 32 | 33 |
| glycerine : n-propanol | 20 | 22 - 23 | 24 - 34 | 35 |
| glycerine : isopropanol | 21 | 23 | 24 - 35 | 36 |

This method of fractionation[72] is also found applicable to palm kernel oil, rice bran oil, tallow, lard and herring oil. The results of the optimum conditions for fractionating these oils are summarized in TABLES 2.2 and 2.3 .

In view of the large number of solvent systems applicable to fractionation by this process, the author chose to study in greater detail one of the systems. The solvent system was water-isopropanol. It was found that using this system, the percentage of olein in the medium was 0.18% and that of the medium in the olein to be 3.39%. This indicates essentially that the medium does not act as a solvent for the oil. Further experiments were carried out to determine the number of times the medium could be re-used for fractionation and it was found that it could be re-used seven times.

The fractionation process can be carried out at any suitable temperature and is independent of the method of crystallisation of the oil. A typical recrystallisation procedure for palm oil consists of heating the oil to 55°C followed by controlled cooling, maintaining $\Delta t = 2^{\circ}C$ ($\Delta t$ being the temperature difference of the oil and the cooling bath) down to the desired temperature for fractionation. Experiments have been carried out to determine the characteristics of the products when recrystallisation and subsequent fractionation were carried out at low temperatures viz. 20°C, 18°C, 16°C and 10°C. The results are given in TABLE 2.4 .

## TABLE 2.2

## CONDITIONS FOR EFFECTING OLEIN-STEARIN SEPARATION OF OILS BY CENTRIFUGATION

| Solvent system | A<br>Crude palm oil (v/v) | B<br>Refined palm oil (v/v) | C<br>Rice bran oil* (v/v) | D<br>Tallow (v/v) | E<br>Lard (v/v) | F<br>Herring oil (v/v) |
|---|---|---|---|---|---|---|
| water : acetone | 35:65 | 36:64 | 34:66 | 35:65 | 38:62 | 35:65 |
| water : ethanol | 43:57 | 43:57 | 42:58 | 46:54 | 44:56 | 41:59 |
| water : n-propanol | 44:56 | 44:56 | 44:56 | 47:53 | 46:54 | 46:54 |
| water : isopropanol | 45:55 | 44:56 | 46:54 | 45:55 | 45:55 | 47:53 |
| propylene glycol : acetone | 36:64 | 38:62 | 38:62 | 33:67 | 35:65 | 34.5:65.5 |
| propylene glycol : butanone | 28:72 | 29:71 | - | - | 32:68 | - |
| propylene glycol : ethanol | 47:53 | 47:53 | 46:54 | 48:52 | 48:52 | 44.5:55.5 |
| propylene glycol : n-propanol | 44:56 | 45:55 | 47:53 | 46:54 | 45:55 | 45:55 |
| propylene glycol : isopropanol | 48:52 | 47:53 | 50:50 | 48:52 | 48:52 | 50:50 |
| glycerine : ethanol | 24:76 | 25:75 | 23:77 | 25:75 | 25:75 | 21:79 |
| glycerine : n-propanol | 22:78 | 24:76 | 22:78 | 21:79 | 22:78 | 25:75 |
| glycerine : isopropanol | 23:77 | 25:75 | 25:75 | 22:78 | 24:76 | 23:77 |

Centrifugation conditions

|  | g | min | °C |
|---|---|---|---|
| A | 2000 | 5 | 25 |
| B | 2500 | 5 | 25 |
| C | 2500 | 5 | 25 |
| D | 2500 | 15 | 25 |
| E | 2500 | 5 | 25 |
| F | 2000 | 5 | 3 |

The volume ratio of oil to solvent system in each case is 1:1

* The separation involves the oil and the wax.