Interchangeability of Fats and Oils

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ABSTRACT

The requirement for interchangeability of fats and oils is a result of such factors as availability and cost of raw materials, and the effects of legislation or market preference on product composition. Such changes should not affect the product's quality or performance. Interchangeability is practiced today in the production of products for human food, animal feed and technical uses, and is frequently controlled by computer.

It is necessary fully to identify a product and its essential features whether simply by melting point or a full triglyceride structure. Modern analytical techniques such as NMR, GC, HPLC and DSC have enabled this identification to become a more exact science.

The interchange may consist of a simple substitution of one oil or fat for another, or it may be more complex, involving a number of oils and fats and processes. Finally, the nature of the product may be such that it has to be "tailor-made" using sophisticated processes to produce the required triglyceride composition. The unit processes which are employed are blending, hydrogenation, fractionation and interesterification. In the last process the recently published use of enzymes is of particular interest.

Problems encountered are mainly concerned with the polymorphism of fats and oils which frequently sets limits on the proportion of a particular fat which can be used. Limits are also imposed by plant processing capacity.

Palm and lauric acid oils are particularly important in the context of interchangeability for both edible and technical purposes because of their fatty acid and triglyceride compositions. They provide good examples of usefulness, problems resulting from polymorphism and the difficulties of substitution.

INTRODUCTION

A provisional figure for the world production of oils and fats in 1983-84 is approximately 62.3 million tons, compared with 65.6 million in 1982-83 (1). This drop in production caused by relative failures of soybean, rapeseed, oil palm and coconut crops was responsible for the considerable increases in across-the-board prices experienced in the latter half of 1983 and continuing to a large extent to the present time. The coincidence of these shortages is unusual, but the effect, increased cost, of individual cases is the reason for the desire for interchangeability or substitutability of oils and fats.

The availability of oils and fats is limited, sometimes totally, by other factors such as:

- legislation, whereby a particular oil may be prohibited,
- religious prohibitions,
- the imposition of tariff barriers.

These and other similar factors limit the possibilities for interchangeability. Other limitations are of a technical or marketing nature such as:

- traditional preferences, for example of flavor or texture,
- changes in market demand, instanced by the growing preference for vegetable oils,
- crop possibilities which are dependent on agricultural conditions,
- economy of throughput because of which, and as a result of low demand, an oil can disappear from a particular market.

The raw materials of interchangebility are the oil types remaining to the processor after the pruning is complete. They vary in chemical composition and physical properties and contain differing levels of impurities which affect their final quality and the processing stages which are needed for their purification. Additives such as emulsifiers, antioxidants, crystal stabilizers and inhibitors should also be considered in this category.

Interchangeability presumes the existence of a product with a certain quality and properties. The invention of margarine in 1869 is an excellent example of the use of technology, in this case fractionation, combined with a cheap raw material to develop a substitute for an existing product. All such investigations must commence with an adequate understanding of the requirements for the product.

The tools used for interchangeability projects are analytical methods, the refining process, blending, hydrogenation, fractionation, interesterification, processing and, to a growing extent, the computer.

PRODUCT IDENTIFICATION

The process begins with setting the product specification. This will include physical and chemical characteristics and quality parameters such as oxidative stability and bakery performance. In most cases the alternative is required to meet the standards of the original but, as in the case of cocoa butter substitutes or the original margarine, a cheaper product of adequate performance will achieve market acceptability. Alternatively, the substitute may out-perform the original as, for example, the development of specialist shortenings for bakery use.

A product is described primarily by its physical characteristics. Thus, a salad oil must satisfy the AOCS Cold Test by remaining "clear, limpid and brilliant" after a minimum of 5½ hours at 0 C and, in many cases, subsequently for a further 72 hours at ambient temperature. Cooking oils, for example palm olein, are frequently judged on their cloud point which is normally less than 10 C and on their smoke point in common with frying fats and oils in general.

The SFC curve is of principal importance in the specification for margarines and shortenings. It should be set for at least four temperatures such as 10, 20, 30, 35 C or 20, 30, 35, 40 C depending on the product. Otherwise, what has been called "slope unawareness" (2) will result if, for example, measurements are taken at only two temperatures. In the cases of specialist fats, such as are used for confectionery and synthetic creams of all types, the SFC is again of importance, but in addition cooling curves or differential scanning calorimetry (DSC) are often required. The solid fat content (SFC) is also important for frying fats which should not leave a greasy or waxy sensation on the palate.

Chemical parameters which are to be specified are the fatty acid composition, particularly for products designated as high in polyunsaturated fatty acids, and the triglyceride composition. The latter is of major importance for cocoa butter substitutes and for the crystal stability of margarines and shortenings during storage. A further factor which must be considered is the desired oxidative stability of the product.

The final part of a product's identification is its performance. Salad oils are basically simple and will be satisfactory if they meet the physical and chemical requirements mentioned in addition to normal quality standards of flavor and color. Frying oils and fats are required to have a frying life the end of which is determined by off-flavor development, darkening, frothing or physical and chemical tests such as the smoke point, acid value, saponification color value or content of oxidized fatty acids (3).

Lubricity (4), which can be loosely interpreted as the state of lubrication, is of prime importance in margarines and shortenings whether they are to be capable of spreading at refrigerator temperatures, creaming for the production of cakes, or being rolled out for the production of puff pastries. Lubricity incorporates ease of handling, separation of gluten in dough and mouth feel. It is, therefore, closely related to the SFC curve by which the plastic range of a shortening and the pleasant, cool manner in which a fat melts in the mouth are in part determined. The other factors which govern this state are the triglyceride composition of the fat and the manner in which it is processed.

PROCESSES

Refining

Edible oils and fats in the crude form contain a wide and variable collection of impurities some of which can have an effect on their use as substitutes for other oils. Of these there are again some which require modification of the refining process or even dictate the type of process to be used.

The two processes in current commercial use are chemical or caustic soda refining and physical refining. Certain oils contain impurities which cannot be removed sufficiently by the pretreatment steps to enable them to be physically refined to the required degree of quality. Examples of this situation arise from the gossypol content of cottonseed oil and the sulphur content of fish oils. These oils can, however, be satisfactorily refined by the caustic soda process. Other oils, due to poor harvesting, extraction or handling, contain high levels of nonhydratable phosphatides, trace metals, oxidation products and pigments, for example chlorophyll, which also result in a deodorized product of unsatisfactory quality by the physical route. Again, in this case a usable oil can normally be prepared using caustic soda refining, albeit with higher costs. In these two cases a refinery equipped solely with the physical refining process is limited in the variety of oils it can handle for interchangeability or is handicapped by variability of deodorized oil quality. Even with good-quality crude oils the nature and content of impurities differ from one oil variety to another, resulting in the necessity to change processing conditions and levels of process chemicals used. These facts should be kept in mind when equipment is being chosen for a refinery.

Hydrogenation

The process which has to date had the greatest effect on the interchangeability of oils is hydrogenation (5). The process has enabled the production of a very large number of alternatives to naturally occurring hard fats. By the use of selective and nonselective conditions fats with, respectively, steep and relatively flat SFC curves are produced which have found universal use in margarines and shortenings.

The oxidative stability of soybean oil is improved by the reduction of linolenic acid content to less than 3% by selective hydrogenation to an iodine value of 110. One million tons per year of fish oil, which in its extracted state contains fatty acids with up to six double bonds in the chains, have been made available to the edible oil industry. By virtue of their wide triglyceride composition resulting from fatty acid chain lengths from C_{14} to C_{22} in significant quantities, hardened fish oils possess useful crystal stabilizing properties and assist in the creaming performance of bakery products.

Simple hard butters, biscuit cream fats and nondairy cream fats can be made by the hydrogenation of coconut, palm kernel and soybean oils.

Fractionation

Fractional crystallization is the oldest of the processes employed for the interchange of oil types. It is also the only presently commercially viable method by which oils and fats can be fractionated.

Dewaxing, which is a special case of the fractionation process, is used for the removal of high-melting waxes from liquid oils such as sunflowerseed and safflowerseed oils (6,7). Such waxes, if allowed to remain in the oil, form an unattractive deposit in bottled oils stored in cool cabinets and refrigerators, and will cause splitting of the emulsion in cooled mayonnaise or salad cream. Dewaxing is frequently included with winterization (7), which was the name given to the separation of high-melting triglycerides from cottonseed oil for the same reasons. The two processes are very similar in technology and indeed in a few cases, for example sunflowerseed oil, waxes and stearin are removed together. There are three methods in use for fractional crystallization (8). These are referred to as the dry (9), detergent or Lanza (10) and solvent (11) processes. The basic technology of these processes has been well reported. They differ in their complexity of operation, cost and integrity of the stearin fraction obtained. Separation of the fractions is governed by crystal formation which governs the occlusion of olein in the stearin phase, and by the difference in viscosity and specific gravity of the phases. The purest stearin is consequently obtained from the solvent process in which the olein is dissolved in hexane, acetone, isopropanol or 2-nitropropane, of which the use of 2-nitropropane will not be permitted in the E.E.C. if a proposed directive (Com[183] 626 Final) is adopted. All of these methods can be used for dewaxing and winterization as well as for the more common fractionation as practiced for palm and palm kernel oils and tallow.

Interesterification

The interesterification reaction as applied to the interchangeability of edible oils and fats is more accurately of two types, acidolysis and ester-ester interchange. The former is the reaction of an oil, fat or blend with a fatty acid such that a proportion of the fatty acid is introduced into the triglycerides of which the oil was composed. Ester-ester interchange involves the rearrangement of fatty acids between esters, for example triglycerides, and is the form in which the reaction is primarily practiced (12).

In the reaction a randomized equilibrium mixture of triglycerides is produced from which this form of the reaction, random, gets its name. If the equilibrium is disturbed by cooling the system such that trisaturated glycerides are crystallized from the liquid phase the process is termed "directed" (13). The effect of randomization on the melting points of certain oils, fats and blends is shown in Table I.

The conventional reaction as described so far is normally conducted at 80 to 110 C under vacuum, using alkali metal or alkali alcoholate catalysts and on an oil that is substantially neutral, with a low oxidation product level and with

TABLE I

Melting Point Changes Due to Random Interesterification (12)

Fat	M.p. C Before	After
Soybean oil	- 7.0	5.6
Cottonseed oil	10.6	34.0
Coconut oil	26.0	28.2
Palm oil	39.8	47.0
Lard	43.0	43.0
Tallow	46.2	44.6
40% Hydrogenated cottonseed oil + 60% coconut oil	57.8	41.1
25% Tristearine + 75% soybean oil	60.0	32.2
25% Hydrogenated palm oil + 75% hydrogenated palm kernel oil	50.2	40.3

a moisture content as low as is practically possible. An extension of the process was patented in 1980 (14,15) in which a hydrolysis catalyzed by enzymes is used to effect the rearrangement. Three types of enzyme have been described according to their specificities. The first group shows no marked specificity, and therefore the products of the reaction are similar to those obtained by the alkali metal or alcoholate catalysts. The second group of enzymes possess 1,3 specificity, that is, they release the fatty acids from the 1- and 3- positions of the triglycerides. If a desired fatty acid is introduced into the system the reaction product will contain triglycerides having the new fatty acid in the 1- and 3- positions. The third group shows specificity towards a particular fatty acid. In this manner, for example, oleic acid can be replaced in a triglyceride by linoleic acid.

Blending

The result of the various processes described is a very large number of oil types ranging from liquid oils which remain clear at refrigerator temperatures to trisaturated glycerides with melting points of about 65 C.

In the blending of these oils to achieve the desired product it is necessary to meet or approximate the specification discussed earlier. In the simplest cases this involves either blending oils, for example, palm olein with rapeseed or soybean oils, to meet a frying or cooking oil specification, or the straight substitution of one hardened oil for another based on an SFC specification.

The blending interchange becomes more complex when, for example, introducing palm olein into a margarine blend in place of soybean oil. A straight substitution is normally not possible in such cases because allowances must be made for the small but significant SFC of palm olein at 10 and 20 C.

In effecting substitutions in margarine and shortening blends it is necessary to consider the crystal habit or tendency of the crystalline form of the oil or fat being introduced and its effect on the crystal form of the product on storage. The beta polymorph is more stable than the beta prime, but the rate of transformation of beta prime to beta differs for individual oil types. Their classification in this respect is shown in Table II. The beta prime form is desired for most margarines and shortenings because of the smooth texture which it gives to the product. It will be noted that palm oil is in the beta prime category but a margarine composed of, for example, palm stearin, palm oil and palm olein will on storage for about two weeks become hard and brittle, a state associated with beta structure. To produce a fat with enhanced beta prime stability it is necessary to avoid a preponderance of one triglyceride or closely similar triglycerides. For this reason variation of fatty-acid chain length by, for example, inclusion of a lauric acid oil or hardened fish oil, or by using 10 to 20% of a C_{16}-containing fat such as hardened palm oil or hardened cottonseed oil is to be recommended. The different configuration of elaidic acid, in middle-melting hardened oils, compared with oleic acid is also of assistance. The excessive presence of one triglyceride can be mitigated by random interesterification, and beta prime stability can also be enhanced by the use of additives such as sorbitan tristearate and diglycerides (16).

TABLE II

Classification of Fats and Oils according to Crystal Habit

Beta-type	Beta prime-type
Soybean	Cottonseed
Safflower	Palm
Sunflower	Tallow
Sesame	Herring
Peanut	Menhaden
Corn	Rapeseed (high erucic acid)
Canola	Coconut
Olive	Palm kernel
Lard	Milk fat (butter oil)
Cocoa butter	Modified lard

TABLE III

Crystallization Rate of Fats (18)

Fat	Time (minutes)	Temperature (° C)
Coconut	3	20
Coconut/palm 1:1	4	15
Coconut/palm, interesterified 1:1	5	18
Palm, hardened	5	17
Palm, hardened/palm 2:1	8	13
Lard	14	10
Lard/palm 1:1	15	10
Palm	27	10
Sheafat	45	10

The most complex form of the blending operation is to be found in the so-called "tailor-made" fats in which a particular composition of triglycerides is required. Such fats, for example cocoa butter equivalents, are built up from a knowledge of the triglyceride composition of individual components obtained by one or more of the hydrogenation, fractionation and interesterification processes.

The computer is proving to be a useful tool in the interchangeability of oils and fats and is being used increasingly for minimum cost blending systems. In these systems the compositional parameters and appropriate physical and chemical data for individual products are stored in the computer together with the results of many trials involving the various oils available on the market. At any time the prices of the individual oils and fats are fed into the computer which will then present one or more formulations with their costs for the final choice to be made by the technical and commercial management. The computer may also be used for calculating the triglyceride composition that will result from the random interesterification of an oil or blend of oils (17). As the number of fatty acids in the system increases the calculations become too complex for human mathematical handling. Finally, when fats are to be tailor-made to a particular triglyceride composition, the possible alternative routes to this composition can be supplied by a computer which holds the necessary compositional data.

Processing and Distribution

With the exception of salad and cooking oils all fat products are subjected to some form of crystallization process before packaging. The rate of crystallization varies between the individual fats as is shown in Table III. This variation must be considered during the chilling process. If crystallization is not virtually complete at the time of packing the heat of crystallization evolved in the package will melt crystals already formed and result in poor product texture. Similarly, when by component substitution a blend is made more prone to formation of beta crystals, close temperature control of the product must be exercised during storage and distribution.

APPLICATIONS

The usefulness of the processes described can be illustrated by examples of their application.

Salad and Cooking Oils

Table IV shows data resulting from the dry fractionation of

TABLE IV

Fractionation of Hydrogenated Soybean Oil, I.V. 105

	Stearin	I.V. 105	Olein
Iodine value	91	104.9	108.3
Yield %	20.5	–	79.5
Cold test (house)	–	–	7
Trans-isomers %	19.2	16.6	14.9
Linolenic acid %	2.3	3.0	3.2

TABLE V

Eutectic Mixtures (20)

Blend (%)		Solid fat index (C)						
Palm oil	Palm kernel oil	10	20	30	35	42	M.p. C	I.V.
0	100	51.2	37.4	1.3	1.0	0	27.5	17.6
20	80	44.2	26.0	1.2	0.8	0	26.8	–
40	60	40.2	18.0	3.1	2.1	0.4	28.8	–
60	40	36.3	12.2	4.6	3.9	1.6	32.0	–
80	20	33.9	14.5	6.3	3.8	0.6	33.0	–
100	0	42.4	21.6	8.4	5.2	0	33.5	52.0

TABLE VI

Interesterification of 20% Palm Stearin, 80% Lightly Hydrogenated Vegetable Oil

	Before	After
SFC @ 10 C	24.4	21.2
20	20.8	12.2
30	12.3	1.5

TABLE VII

Solid Fat Contents (%) of Refined, Hydrogenated and Interesterified-Hydrogenated Coconut and Palm Kernel Oils

	Coconut oil			Palm kernel oil		
	Refined	Hydrog.	Inter hydrog.	Refined	Hydrog.	Inter hydrog.
SFC @ 10 C	59	62	54	48	72	68
21.1	29	38	37	31	65	57
26.7	0	10	17	11	49	42
33.3	0	2.5	0	0	22	12
37.8	0	0	0	0	9.5	0
Wiley M.p. C	24.4	36.7	31.7	28.3	44.4	35.0

a lightly and selectively hydrogenated soybean oil. By this means a salad oil of acceptable cold test and of improved oxidative stability compared to the starting oil is obtained (19). A double fractionation of IV77 HSBO reported in the same paper yielded a first stearin which can be used as a margarine or shortening hardstock, a second stearin or mid-fraction with an SFC curve suitable for use as a hard butter and an olein fraction which has the properties of a cooking oil of very high oxidative stability.

Margarines

In the blending of margarines the eutectic softening effect (Table V) seen at the low temperature end of the SFC curve of mixtures of palm oil and lauric fats can prove useful (20). Table VI demonstrates that the random interesterification of a blend of 20% palm stearin with 80% lightly hydrogenated vegetable oil can produce a stock for use in refrigerator margarine (13). Among other examples cited for the use of random interesterification for margarines is the preparation of a blend consisting of a hardstock obtained by the randomization of a blend of 30% palm oil, 30% palm stearin (melting point 55 C), 40% palm kernel oil which is mixed 1:1 with liquid vegetable oils containing high levels of polyunsaturated fatty acids (21). Another example utilizes co-randomized blends of palm oil, palm stearin and soybean oil at about 80% level with 20% of blended palm oil, palm olein and hardened palm oil (22).

Hard Butters

Table VII gives examples of the hard butters or cocoa butter substitutes obtainable from lauric oils by hydrogenation alone or by interesterification of the hydrogenated product. Such products can be adjusted to climate or use by blending of the starting material and randomized product (23) or by co-randomizing with a high melting point vegetable fat.

THE FUTURE

The future of interchangeability of oils and fats lies primarily in the development of the techniques outlined in this paper with emphasis on assistance from computer formulation. Possibilities for the application of biotechnology in this field are particularly interesting. Perhaps a practical dehydrogenation method will be developed by this means.

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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).

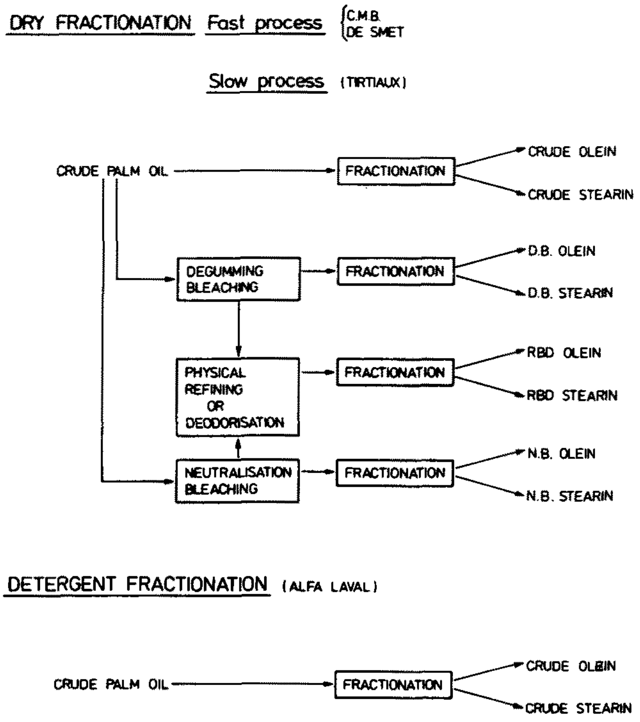

FIG. 1. Integration of fractionation process in the refining cycle.

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