# Interesterification of Edible Oils

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## ABSTRACT

Types of interesterification discussed are (a) interchange between a fat and free fatty acids, in which the most important reaction is the introduction of acids of low mol wt into a fat with higher fatty acids; (b) interchange between a fat and an alcohol, e.g., with glycerol, in order to produce emulsifiers like monoglycerides; (c) rearrangement of fatty acid radicals in triglycerides, the so-called transesterification which in recent years has taken on the same importance as hydrogenation or fractionation. In natural fats, the fatty acid radicals are not usually randomly distributed but become so by rearrangement; the distinctive physical properties of natural fats and oils can be changed within limits by this transesterification. Well-known examples are cocoa butter, palm oil, and lard. More important is the transesterification of a mixture of different fats and oils; e.g., the combination of hydrogenation and interesterification allows the production of a solid fat with high linoleic acid content. The composition of glycerides after random interesterification can be calculated by formulas.

Distinct from random is such directed interesterification. This is done by working at low temperatures that glycerides with higher melting point crystallize from the reaction mixture. Directed interesterification can be combined with fractionation, for instance, to get a higher yield of liquid fraction from palm oil than is obtained by fractionation alone.

The transesterification process can be performed in a batch or continuously. A small amount of metallic sodium or sodium ethylate is used as catalyst, which is destroyed by water or acid and removed after the reaction.

Since 1950, the importance of the interesterification process has grown continuously, and today it is used as frequently as hydrogenation in many areas.

The term *interesterification* refers to that reaction of fats and oils in which fatty acid esters react with other esters or fatty acids to produce new esters by an interchange of fatty acid groups. It is this part which I will describe, and no reference will be made to reactions of fatty acid esters with alcohols.

Since the fatty acid distribution in fats can be changed by interesterification, I will first briefly discuss the possible distributions of the fatty acids in triglyceride molecules. For this purpose, I will assume the simple case that we have only two different types of fatty acids, namely, saturated (S) and unsaturated (U). The minimum distribution as shown in Figure 1 is the simplest possibility. For instance, a composition which consists of 1/3 saturated and 2/3 unsaturated fatty acids is considered to be a mixture of only two types of glycerides, of which 1/3 is $GS_3$ (glyceride with three saturated acids) and 2/3 is $GU_3$ (glycerides with three unsaturated acids). Another simple distribution is the even distribution (Fig. 2). In the example of 1/3 S and 2/3 U, there is only one type $GSU_2$. In another example of 1/2 S and 1/2 U, the composition is 1/2 $GSU_2$ and 1/2 $GS_2U$.

Random distribution is most frequent because in a liquid phase the normal ester rearrangement or esterification of acids with glycerine proceeds at random with the attainment of an equilibrium composition, which in our simple case of only two types of fatty acids can be calculated by using the formulas shown in Figure 3. Figure 4 shows the curves of these formulas. For instance, 50% S and 50% U give 12.5% $GS_3$, 12.5% $GU_3$, 37.5% $GSU_2$, and 37.5% $GS_2U$.

At this point, reference should be made to isomerism. In

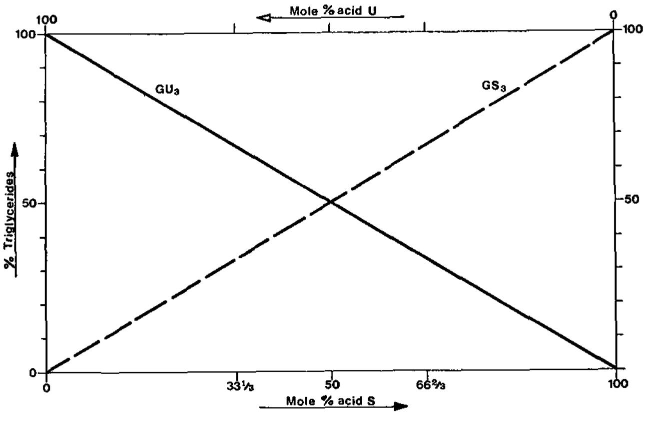


FIG. 1. Minimum distribution of fatty acids. S = saturated and U = unsaturated fatty acids.

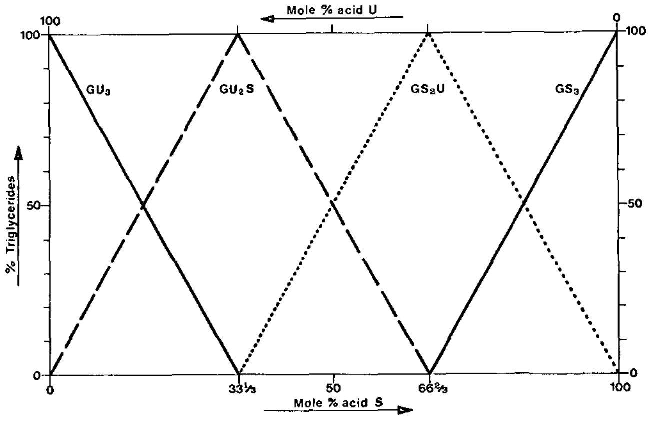
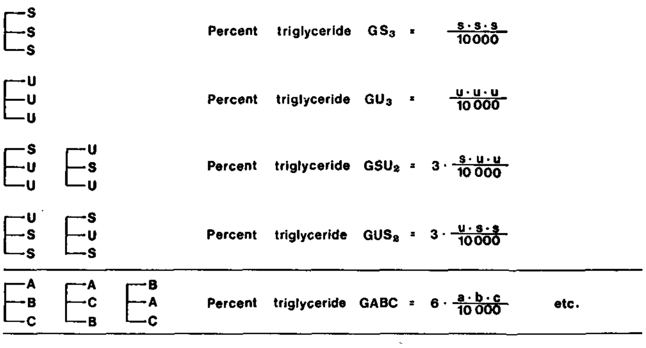


FIG. 2. Even distribution of fatty acids. S = saturated and U = unsaturated fatty acids.



Percent triglyceride $GS_3 = \frac{s \cdot s \cdot s}{10000}$

Percent triglyceride $GU_3 = \frac{u \cdot u \cdot u}{10000}$

Percent triglyceride $GSU_2 = 3 \cdot \frac{s \cdot u \cdot u}{10000}$

Percent triglyceride $GUS_2 = 3 \cdot \frac{u \cdot s \cdot s}{10000}$

Percent triglyceride $GABC = 6 \cdot \frac{a \cdot b \cdot c}{10000}$ etc.

FIG. 3. Formulas for calculating the random distribution of fatty acids. s,u,a,b,c = molar percentages of the fatty acids S (saturated), U (unsaturated), A, B, and C; G = glycerine.

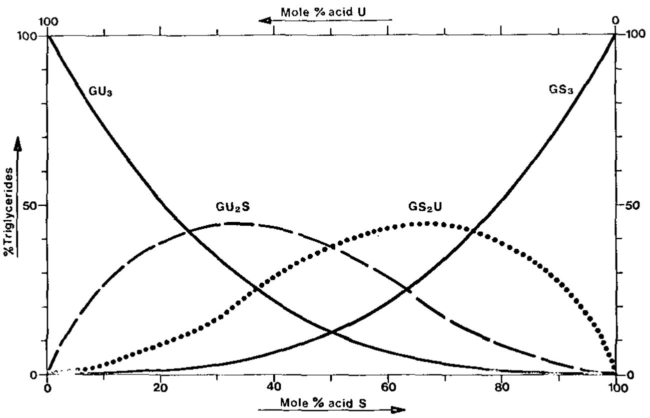


FIG. 4. Random distribution of fatty acids. S = saturated and U = unsaturated fatty acids.

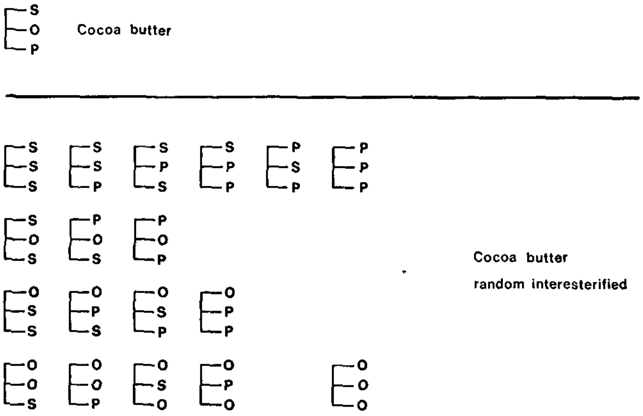


FIG. 5. Glyceride structure of cocoa butter before and after random interesterification.

the glyceride $GS_2U$, the unsaturated acid could be located in two different positions: the middle $\beta$-position (2) or the $\alpha$-position (1). After interesterification of an ester, the random distribution occurs whereby in the molecule type $GS_2U$ 2/3 of the unsaturated acid appears in position 1 and 1/3 in position 2.

Cocoa butter is a typical example in this respect (Fig. 5). The fatty acid composition consists of ca. 2/3 saturated acids (stearic and palmitic acids) and 1/3 unsaturated acids. The glyceride composition of the natural cocoa butter may be called an even distribution because it contains mainly glycerides with one unsaturated acid in position 2 and two saturated acids in position 1. This is the explanation for the unusual physical behavior of cocoa butter. By interesterification cocoa butter will lose these typical properties because the fat then has a random distribution with only a slight amount (12.5 %) of the original cocoa butter glycerides. Therefore, cocoa butter cannot be produced by interesterification or by esterification of the correct fatty acid composition.

Before uses of the interesterification process can be discussed, some mention must be made of the technological procedure. Interesterification may proceed in two ways: random or directed. Both procedures may be carried out in a discontinuous or in a continuous way.

When random rearrangement is preferred, the fat is heated to ca. 80 C in the presence of a catalyst and with rapid stirring for half an hour. The most common catalysts are sodium methylate or sodium-metal. It is essential that the fat contain no substances which destroy the catalyst. The amount of catalyst required depends upon several factors. If the water content is $< 0.01\%$, the free fatty acid level below 0.05%, and the peroxide content is also very low, the addition of only 0.1% of catalyst is sufficient. Therefore, the fat must be well refined, dried, and heated to 150 C under a nitrogen blanket before the catalyst is added. Experience indicates that the addition of each additional 0.1% catalyst results in a loss of ca. 1% neutral fat.

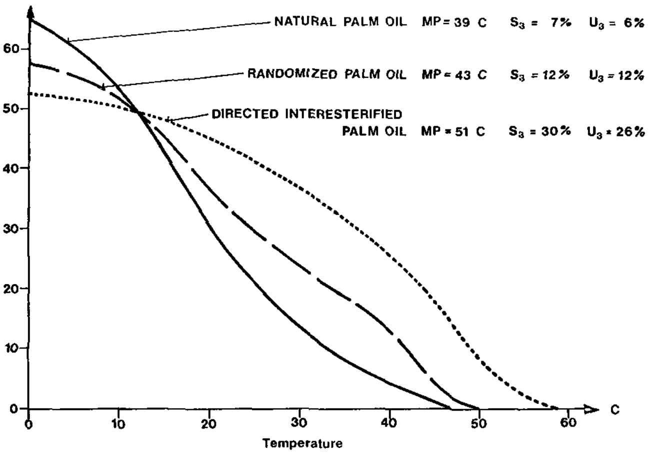


FIG. 6. Solid fat index of palm oil before and after interesterifications. S = saturated and U = unsaturated fatty acids.

When the directed interesterification process is applied, some of the fatty acids or their glycerides are removed from the equilibrium reaction. The procedure commonly used is to continuously distill the acids with low mol wt from the fat, such as a mixture of coconut oil with an excess of free fatty acids, or, even more important, the interesterification is carried out at such low temperatures that higher melting glycerides which are formed by the interesterification get separated from the residual liquid phase after crystallization. During rearrangement and continuous crystallization, the formation of an increasing amount of high melting glycerides occurs. This does not result in random interesterification but, more or less, the minimum distribution of fatty acids in which a mixture of glycerides exists containing saturated and unsaturated acids as mentioned above.

Since the rate of the reaction is slow due to the low temperature, and since the fats tend to supercool, the reaction time is longer than for nondirected interesterification reactions. The reaction time required could be 1 day, and the process is, of course, expensive. Sodium methylate or a liquid alloy of sodium–potassium is used as catalyst. At the end of the reaction, the catalyst must, of course, be inactivated with water or dilute acid before the fat will be heated or the solids will be separated.

In many cases, the directed interesterification increases the melting point, since the melting point of a fat depends to some degree upon the content of saturated glycerides. By this method it is possible to convert a liquid oil into a plastic product with the consistency of a shortening. Directed interesterified sunflower oil has a melting point which is slightly below 20 C and a solid fat index of 10 at 0 C and of 5 at 15 C. If this fat is blended with 5% hardstock of hydrogenated oil, a solid fat with $> 60\%$ essential fatty acids can be produced.

A winterized oil which contains no linolenic acid can be produced by hydrogenation and directed interesterification followed by a fractionation. The yield of the liquid phase from directed interesterified palm oil is higher than from untreated oil, as shown in Figure 6. The soap, which is formed by destroying the catalyst with water, can be used in the fractionating step as tenside.

Since the distribution of fatty acids in most of the natural fats and oils occurs not at random, the nondirected interesterification also changes the distinctive physical properties of the fats, such as the melting point, the solid fat index, the crystallization tendency, the texture, etc. The graininess of ordinary lard is due to large crystals of disaturated glycerides (OPS), in which the palmitic acid is in the 2 (middle)-position and the oleic acid in the 1-position (OPS). Random interesterification reduces the amount of

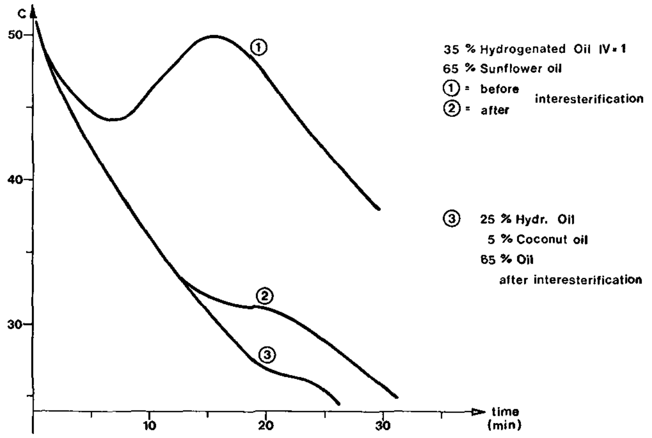


FIG. 7. Solidification curves of sunflower and coconut oils interesterified with hard fats.

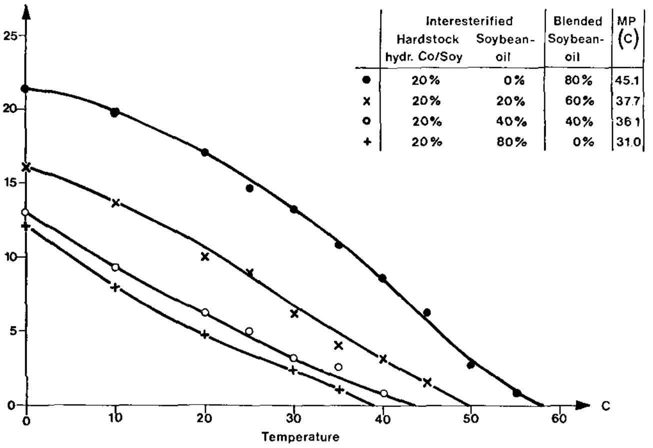
these glycerides. In this case, directed interesterification will eliminate the graininess and simultaneously create a hardstock, so that soft lard will become an improved shortening.

A hard butter with a low melting point (32 C) and also with sharp melting characteristics is obtained by random interesterification of a hydrogenated lauric oil with the melting point of 40-42 C.

Use of interesterification of fat and oil mixtures in the industry is very important and is extremely versatile. It is impossible to describe all the possible applications. However, I would like to explain some typical examples.

One principal advantage of interesterification is that use of this process allows the combination of the properties of different fats and oils. Many of these interesterified fat mixtures are used in margarine and shortening.

Lauric oils, such as palmkernel and coconut oil, have low melting points and short plastic ranges; a margarine with high content of these fats will be very hard if kept in the refrigerator but will melt partly at room temperature. If it becomes desirable to use a large percentage of coconut oil in margarine—and, according to the present low price of coconut oil, one must—the glycerides with three lauric acid moieties must be removed or decreased. This is possible by interesterifying the coconut oil with another type of fat—for instance, with palm oil. Thereby, a margarine may be produced which consists of 60% of the interesterified palm oil—coconut oil mixture, which is then blended with 40% of an oil, e.g., sunflower oil.



| | Interesterified | | Blended | MP |
|---|---|---|---|---|
| | Hardstock hydr. Co/Soy | Soybean-oil | Soybean-oil | (C) |
| ● | 20% | 0% | 80% | 45.1 |
| x | 20% | 20% | 60% | 37.7 |
| o | 20% | 40% | 40% | 36 1 |
| + | 20% | 80% | 0% | 31.0 |

FIG. 8. Solid fat index (%). Hydr. Co = hydrogenated coconut oil.

Interesterification is especially useful when it is desired to combine solid and liquid fats. Many patents relate to fats or margarines having a high polyunsaturated (linoleic) fatty acid content. In these products, the solid fat fraction used could be animal fats, hydrogenated fats, palm oil, or synthetic tristearin. The effect of interesterification can be seen in Figure 7. This shows the solidification curves of a mixture of a hydrogenated oil having a melting point of 70 C and a liquid oil before and after interesterification. The congeal point decreases from 50 C to 31 C.

The solid fat indices of an interesterified hardstock of hydrogenated soybean oil and coconut oil blended with 80% liquid oil are shown in Figure 8. Increasing the percentage of oil before and simultaneously decreasing the percentage after interesterification causes the melting point and the solid fat index to drop. This blended fat represents a good margarine having a high content of essential fatty acids and a low content of *trans*-double bonds.