Interesterification of Fats

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ABSTRACT

Interesterification changes the distribution of the fatty acids among the glycerides of fats or mixtures of fats from what was present originally. This affects the physical nature and behavior of fats. A discussion of this process from the standpoints of mechanism, catalysts, methods of monitoring the reaction and applications will be presented.

INTRODUCTION

Fats and oils play an important role in human diet. Besides providing calories, they act as vehicles for such vitamins as A, D, E and K. They are also the source of essential fatty acids such as linoleic, linolenic and arachidonic acids. They have the unique quality of improving palatability of foods. Because of this they are extensively used in a wide variety of foods. These uses demand widely varying crystallization and melting behavior. The main component of fats and oils is the triester of glycerol and fatty acids (triglycerides). The physical nature of any fat or oil is determined by: a) the chain length of the fatty acids; b) unsaturation of the fatty acids, and c) their distribution among the three hydroxyl groups of glycerol. Generally, those fats that have a high proportion of saturated fatty acids are solid at ambient temperatures, and those in which the unsaturated fatty acids are preponderant are liquid. Nature endows every oil and fat with a certain distribution pattern of fatty acids among the glycerides which also determines their consistency as either solid or liquid. Because of this distribution, the use of any given oil or fat is limited. In order to extend their uses, such processing steps as fractionation, hydrogenation and interesterification, or a combination of these, are usually applied. Fractionation separates an oil or fat into a solid and liquid fraction, each of which can be used separately. Hydrogenation converts a liquid oil into a semisolid or solid fat, thus extending its use. Interesterification alters the original order of distribution of fatty acids in the glycerol moiety producing fats with different melting and crystallization characteristics than the parent. The conditions that allow interesterification to occur, changes effected by this process and some applications are described in this paper.

COMPOSITIONAL CHANGES

Interesterification can be visualized as a break up of a specific glyceride, removal of a fatty acid at random, shuffling it among the rest of the fatty acid pool and replacement at random by another fatty acid. Taking SOL as a typical glyceride, these changes are pictured in Figure 1. The first change shown is a shuffling of the fatty acids within the same molecule. This is referred to as *intraesterification* and, as seen, produces isomers of the same glyceride. As the reaction proceeds further, these new glycerides also participate in the reaction and produce a complex mixture of glycerides as shown. The reaction ultimately attains an equilibrium when all possible combinations of glycerol and fatty acids have taken place. This process is called *interesterification,* and because of the random rearrangement of the fatty acids of the parent oil, it is also commonly referred to as *randomization.* The equilibrium referred to above may be simplified and represented as follows:

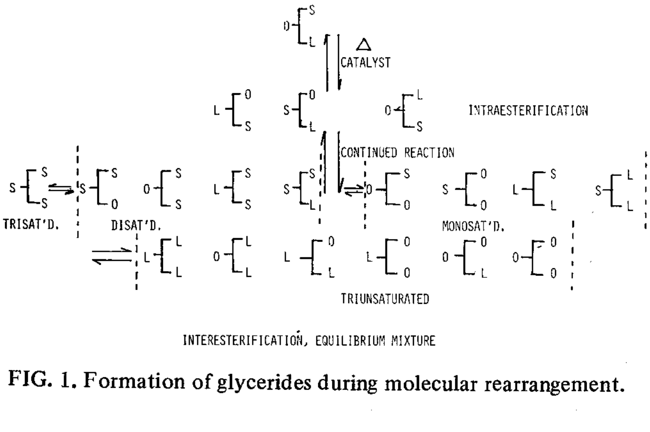


FIG. 1. Formation of glycerides during molecular rearrangement.

$$\mathrm{SSS} \rightleftharpoons (\mathrm{SUS} \rightleftharpoons \mathrm{SSU}) \rightleftharpoons (\mathrm{SUU} \rightleftharpoons \mathrm{USU}) \rightleftharpoons \mathrm{UUU}$$

where S is a saturated acid and U is an unsaturated acid. It should be noted that within each type there are other equilibriums as shown with their respective isomers. The composition of such a randomly rearranged oil or fat can be calculated from probability considerations (1). If A,B, C are the molar percentages of fatty acids A,B,C, then molar percentage of glycerides containing only one acid is:

$$\%\,\mathrm{AAA} = \mathrm{A}^3{:}10{,}000$$

molar percentage of glycerides containing two acids is:

$$\%\,\mathrm{AAB} = 3\mathrm{A}^2\mathrm{B}{:}10{,}000$$

and molar percentage of glycerides containing three acids is:

$$\%\,\mathrm{ABC} = 6\mathrm{ABC}{:}10{,}000$$

The use of these formulas for the example shown in Figure 1 where equimolar percentages of stearic, oleic and linoleic acids are present results in the following glyceride composition for the final randomized equilibrium mixture:

Stearic-stearic-stearic = (33.3x33.3x33.3):10,000 = 3.7%
Oleic-oleic-oleic = (33.3x33.3x33.3):10,000 = 3.7%
Linoleic-linoleic-linoleic = (33.3x33.3x33.3):10,000 = 3.7%
Stearic-stearic-oleic = (33.3x33.3x33.3)3:10,000 = 11.1%
Stearic-stearic-linoleic = (33.3x33.3x33.3)3:10,000 = 11.1%
Stearic-oleic-oleic = (33.3x33.3x33.3)3:10,000 = 11.1%
Stearic-linoleic-linoleic = (33.3x33.3x33.3)3:10,000 = 11.1%
Oleic-oleic-linoleic = (33.3x33.3x33.3)3:10,000 = 11.1%
Oleic-linoleic-linoleic = (33.3x33.3x33.3)3:10,000 = 11.1%
Stearic-oleic-linoleic = 33.3x33.3x33.3)6:10,000 = 22.2%

An experimental confirmation of the statistical composition resulting from randomization was obtained by reacting an equimolar mixture of tristearin and triolein (2).

CATALYSTS

Interesterification of fats can occur at high temperatures as 300 C and higher, but require an inordinately long time and is usually accompanied by decomposition and polymerization. Catalysts speed up the reaction and lower the temperature of reaction. In the early investigations (1,9), metal salts such as zinc chloride, stannous oxide, etc. were used but were soon replaced by alkali metal alkylates (12,13) and alkali metals (9,10,11) as the preferred catalysts. Table I summarizes information on some important catalysts and conditions for their use. It is noted that the catalyst level, time and temperature of reaction vary widely. The most

TABLE I

Catalysts For Interestericiations

Catalysts	%	Temp C	Time	Reference
Metal Salts				
Acetates, carbonates Chlorides, nitrates, oxides of SN, Zn, Fe Co and Pb	0.1-2	120-260	0.5-6 hr under vacuum	3
Alkali Hydroxides				
NaOH, KOH, LiOH	0.5 to 2	250	1.5 hr under vacuum	4,5
Alkali hydroxide + Glycerol	0.05 to 0.1 0.1 to 0.2	60-160	30-45 min under vacuum	6
Metal soaps				
Sodium stearate Glyceride	0.5 to 1	250	1 hr under vacuum	1,5,8
Li Al Stearate Na Ti Stearate	0.2	250	1 hr under vacuum	7
Alkali metals				
Na, K, Na/K alloy	0.1-1	25-270	3-120 min	9,10,11
Metal alkylates				
Sodium methylate Ethylate, t-butylate, etc.	0.2-2	50-120	5-120 min	12,13,14
Metal hydrides				
Sodium hydride	0.2-2	170	3-120 min	15
Metal amide				
Sodium amide	0.1-1.2	80-120	10-60 min	16

widely used of these are the alkylates of sodium, followed by the metals sodium, sodium/potassium alloy and the hydroxides of sodium or potassium in combination with glycerol.

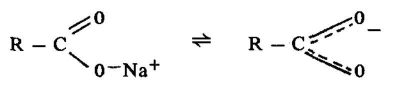
The alkylates of sodium (methylate, ethylate, etc.) are either used as a dry powder or as a dispersion in solvents such as xylene. They are handled easily, low priced, start the reaction at low temperatures such as 50-70 C and can be used in very low levels (0.1%) if the starting oil is well refined and dry. The average use range is 0.2-0 4%. They can be easily removed after the reaction by a water wash. The disadvantages are: the quality of the catalyst varies widely (from batch to batch); after the addition of the catalyst there is usually an induction period before the reaction sets in, and there is a loss of oil due to the formating soap and methyl esters. The metals (Na,K) need costly equipment to handle them. The Na/K alloy, being a liquid, is easy to handle but is more expensive than sodium. Sodium melts at about 98 C and is active at about 120 C. They react with traces of water or hydroxyl containing material in the oil, liberating hydrogen. If the metal droplet is enveloped in the gas, it is rendered useless as a catalyst. Deactivation after reaction is accompanied by generation of heat and gas (hydrogen) formation, and if not carefully handled, it is potentially explosive. The oil or fat must be bone dry before the addition of the metal which is usually used at low levels such as 0.05 to 0.1% by weight of the oil. The onset of the reaction is almost instantaneous with the addition of the metal and is complete in as short a time as five min. (17). The loss of oil is usually low.

The cheapest catalyst is the alkaline hydroxides (KOH or NaOH) in combination with glycerol. Since this process uses an aqueous solution containing the hydroxide and glycerol, it is easier to handle. Sufficient quantities of the hydroxide to neutralize any residual free fatty acid can be used. The disadvantages are that it is a two stage reaction, one at low temperature 60 C under vacuum to neutralize the fatty acid, to remove the water rapidly, and to disperse the hydroxide, and the second at higher temperature, 140-160 C for the interesterification. Glycerol is necessary for the reaction to occur and usually results in the formation of small amounts of partial glycerides (18).

MECHANISMS

When sodium methylate powder is dispersed in a previously dried oil maintained at about 60-80 C, a white slurry is obtained. After heating for a while, the color of the mixture becomes brownish, indicating on onset of interesterification. This change of color is associated with the active catalyst formation, which is visualized as a reaction complex between the added catalyst and the triglyceride. Thus, the methylate or any such added reagents act as initiators, and the true catalyst is the reaction complex. Two mechanisms, one postulating the formation of an enolate ion (19) as an intermediate by the action of the initiator on the glyceride, and another postulating an addition complex of the initiator with carboxyl of the glyceride (17), have been proposed. The enolate ion formation and its hypothesized mode of action to induce intra and interesterification are shown in Figures 2, 3 and 4. It is noted that in both reactions a beta keto ester (structures III and VIII) intermediate is postulated. Evidence for its formation is presented by the appearance of an infrared absorption peak at about 6.4 u, both in the reaction mixture and in the foots removed from this mixture after terminating the reaction by the addition of water.

It may be pointed out that 6.4 u is also the region of absorption due to ionized carboxyls, as would be produced by soaps (20).



Na^3 Ionized Carboxyl

Thus the enolate ion and other ionic intermediates involving ionized carboxyl can cause absorption at 6.4 μ. Numerous exchange reactions between other intermediate

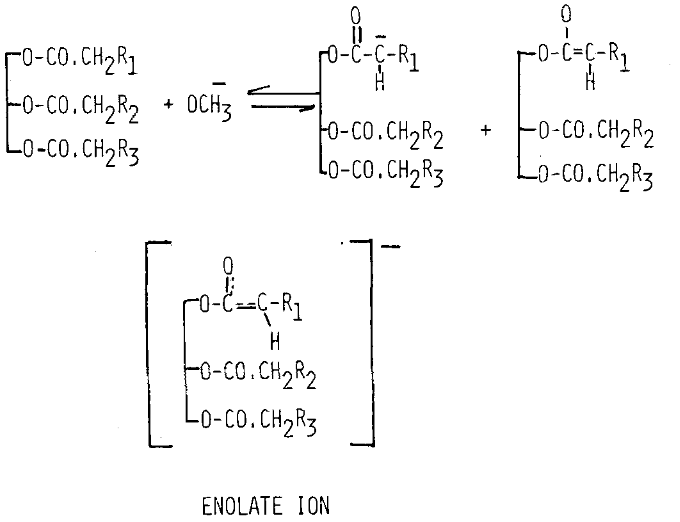


FIG. 2. Endate ion formation.

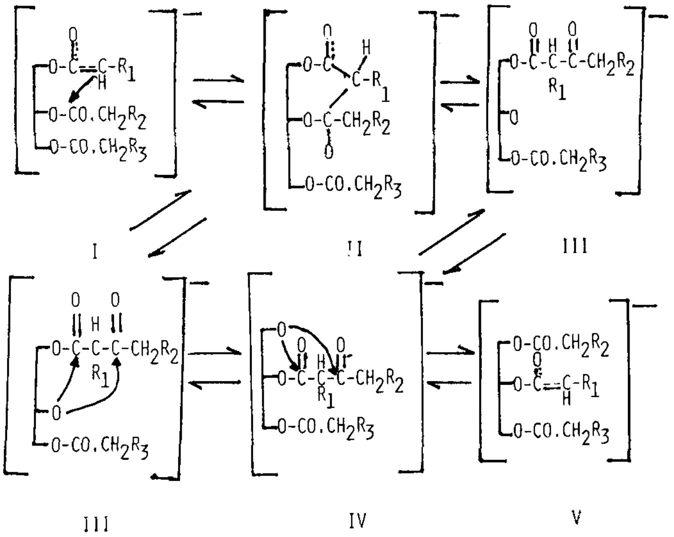


FIG. 3. Mechanism for intramolecular ester - ester interchange.

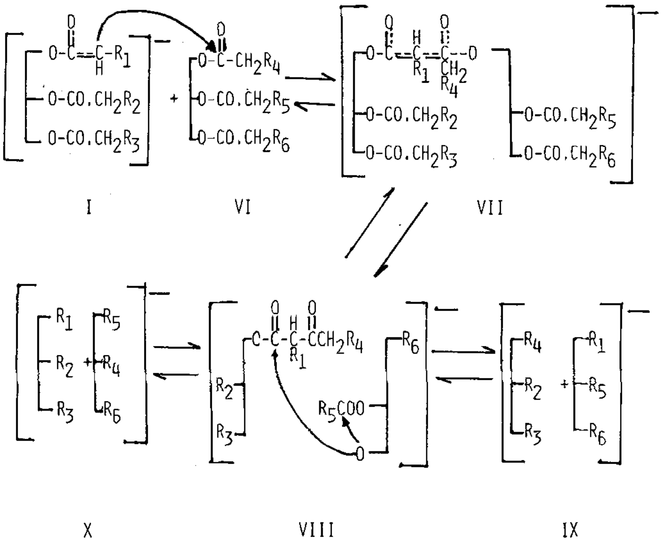
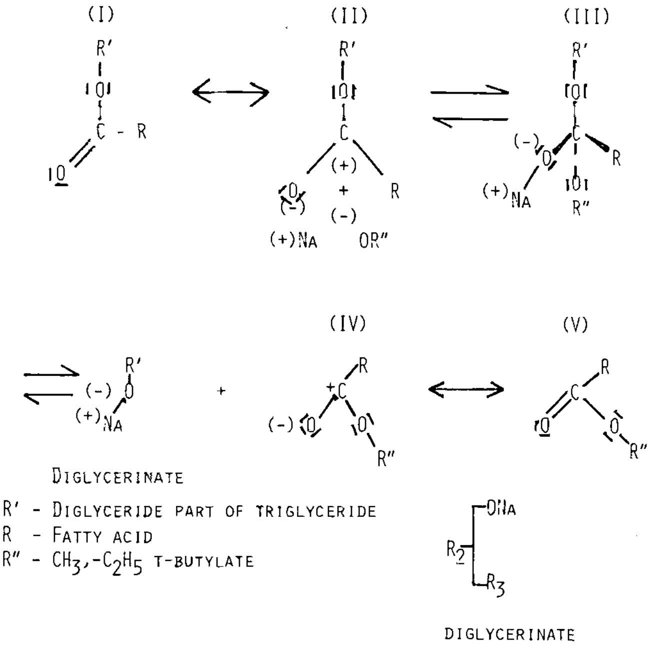


FIG. 4. Mechanism for intramolecular ester-ester interchange.



DIGLYCERINATE

R' - DIGLYCERIDE PART OF TRIGLYCERIDE

R - FATTY ACID

R" - CH_3,-C_2H_5 T-BUTYLATE

FIG. 5. Mechanism of interesterification carbonyl addition.

ionic species are postulated before the final randomized equilibrium mixture is produced. In the other mechanism, Figure 5, the alkylate ion adds on to a polarized ester carboxyl producing a diglycerinate intermediate which would react with another glyceride by abstracting a fatty acid forming a new triglyceride and regenerating the diglycerinate. This process would continue through a series of chain reactions until all available fatty acids have exchanged positions and an equilibrium composition of glyceride mixture is achieved. This interchange for a simple mixture of S3 and U3 is presented in Figure 6.

It should be understood that both these mechanisms are only postulates lacking hard experimental support. They suggest pathways by which the shuffling of fatty acids occur among the glycerides. They have elucidated that an active intermediate is involved, that this intermediate is ionic in nature and the ester interchange is homogeneously catalyzed by this active catalyst. However, the intermediate responsible for the color change and a suitable method to track it down remains to be investigated. The information gained so far indicates that the formation of this intermediate is a slow one, but the fatty acid interchange catalyzed by it is a fast one. That this exchange is fast is also supported by a very short reaction period (as low as 3-5 min) reported by several investigators (9-17) for the attainment of equilibrium.

METHODS FOR DETECTING END-POINT

The visual change that occurs in an interesterifying mixture is the development of a brown color which deepens as the reaction progresses. Usually the reaction is allowed to proceed for a fixed period of time such as half an hour to an hour after the appearance of this color before termination. This procedure, though practical, has not been satisfactory, and many detection techniques have been applied to study interesterification; a few of these will be discussed.

Melting Point

Among the earliest techniques and perhaps the quickest one is the determination of the melting point before and after the reaction. Examination of some of the melting points listed in Table II shows that with vegetable oils there

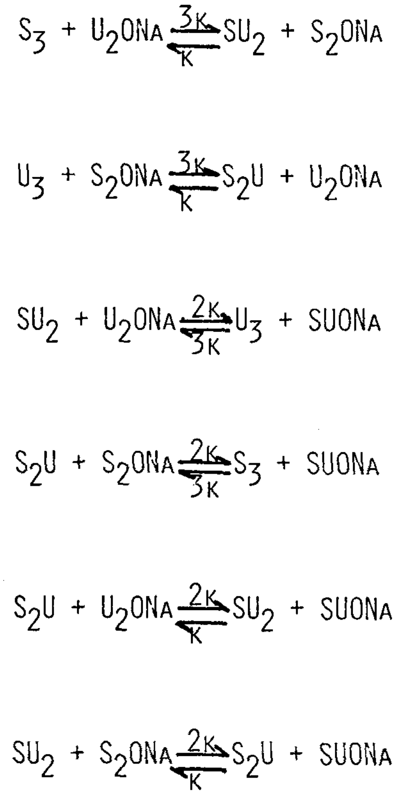


FIG. 6. Chain reaction initiated by diglycerinate for fatty acid interchange.

TABLE II

Melting Point Changes Due to Interesterification (1)

	M.P. F	
Fat	Before	After
Soybean oil	19.4	41.9
Cottonseed oil	50.9	93.2
Coconut oil	78.8	82.8
Palm oil	103.7	116.6
Lard	109.4	109.4
Tallow	115.2	112.3
40% Hydrog. cottonseed oil + 60% coconut oil	136.0	106.0
25% Tristearine + 75% Soybean oil	140.0	90.0
25% Hydrog. palm oil + 75% Hydrog. palm kernel oil	122.3	104.5

is an increase in melting point after the reaction; with animal fats there is no change and with corandomizing mixtures there is a decrease. Thus it is necessary to establish beforehand the pattern of melting point changes and then determine its suitability. In some cases the changes involved may be so small that they may be within the range of experimental error. Though melting point is an easily adopted method, it is not accurate enough.

Dilatometry

The changes in S_3 and S_2U glycerides brought about by interesterification are reflected in the solid contents before and after the reaction. Industry has relied heavily on the SCI values, as these demonstrate better the crystallization behavior. Fig. 7 illustrates the effect of randomization on cocoa butter. A fat with sharp melting characteristics and steep SCI curve is converted into one with a wider melting range and flat SCI curve. Formation of higher melting glycerides due to randomization is shown by the presence of solids even at 50 C. Thus while cocoa butter will melt completely in the mouth, randomized cocoa butter will not. The opposite effect is shown in Fig. 8 for corandomization. Before reaction, the mixture was high proportion of higher melting glycerides due to the palm stearine, but after the reaction their levels are reduced and mixed glycerides containing unsaturated fatty acids are formed. These changes are reflected in the lowering of SCI values at higher temperatures and complete disappearance of solids at about 50 C. A slow melting, and pasty tasting mixture is converted into one with a sharper melting and clean tasting product. In Table III are listed some more examples (21,22,23,24) showing application of SCI to interesterification. Palm oil behaves in the same way as cocoa butter by producing increased amounts of solids at higher temperatures. Lard and tallow show very little change in solids, and thus dilatometry may not be a useful technique with them. With corandomizing mixtures there is little change at 10 C, and a moderate increase or decrease at 20 C depending upon the proportion and nature of the hard component. However, there is a significant decline or disappearance of solids at 35 C, and this can be taken as indicative of the endpoint of interesterification. Dilatometry requires measurements at several temperatures for definitive answers and is time consuming. Attempts have been made to measure solid contents by N.M.R. (27,28), and hopefully a speedier procedure using this technique will be available soon.

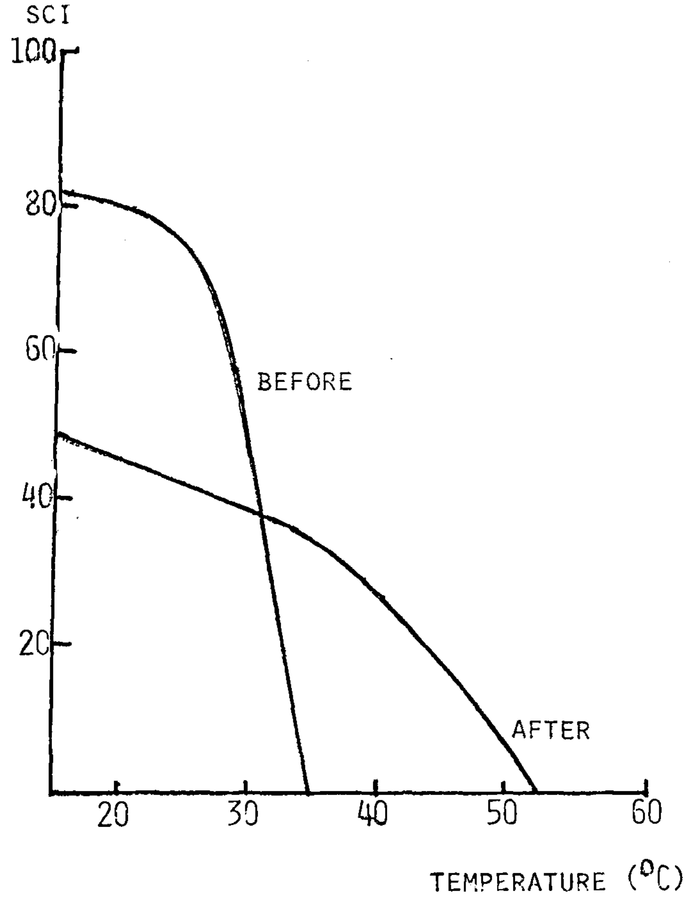


FIG. 7. Solid content index of cocoa butter before and after interesterification.

Glyceride Compositional Analysis

The basic change that occurs due to interesterification is on the glyceride composition. Therefore, knowledge of glyceride composition will aid to understand the reaction

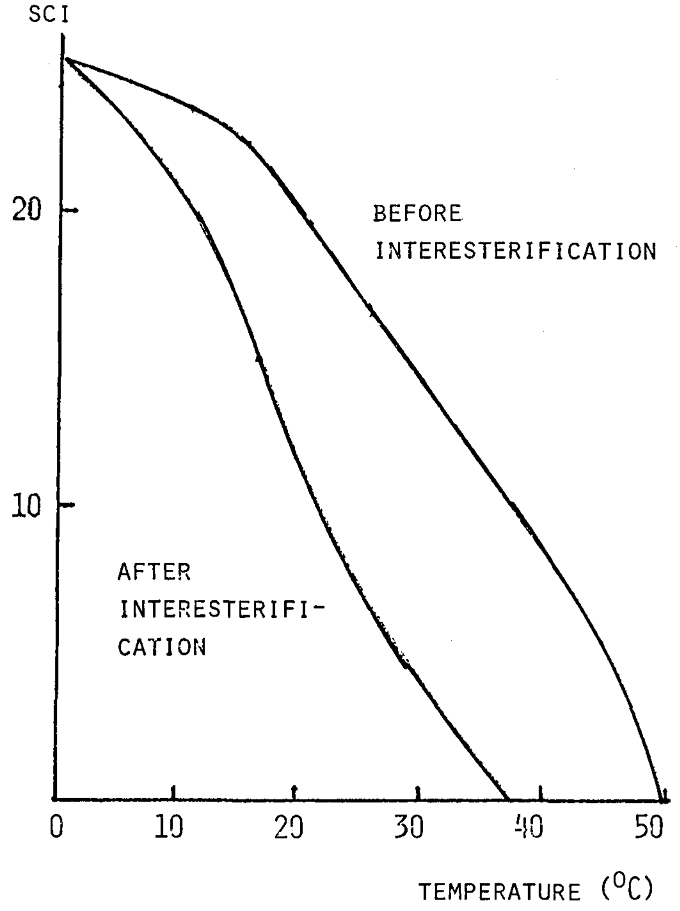


FIG. 8. Effect of randomization on sci of a 80:20 mixture of lightly hardened oil and palm stearine.

better. Several methods of glyceride analysis such as thin layer chromatography (29,30), gas liquid chormatography (26,31), mass spectrometry (32) and pancreatic lipase analysis (33,34) have been applied to study interesterification. These studies have confirmed that both intra and interesterifications do take place and that at equilibrium the postulated statistical distribution of fatty acid is achieved.

Thin Layer Chromatography

The interesterification of such pure glycerides as POP and POS was studied (29) by means of silver nitrate complexed thin layer chromatography. This technique separates glycerides according to their unsaturation. The formation of SU_2 glycerides showed that with both Sodium and Sodium ethoxide catalysts (Table IV), the equilibrium is attained in a little over 45 min. A similar study (29) on the course of corandomization of 60% sunflower oil and 40% fully hydrogenated lard showed (Table 5) the fast disappearance of trisaturated glyceries and the concurrent formation of disaturated linoleo glycerides (S_2L). Thus, in this case following the disappearance of S_3, it can be concluded that when it reaches a minimum the reaction is completed. Confirmation of the fact that a random distribution of fatty acids is taking place is furnished by the increase in the amounts S_2L, SOL and SLL at the expense of S_3, OLL and LLL glycerides.

Gas Liquid Chromatography (GLC)

GLC effects separation on the basis of carbon numbers and thus finds application where lower chain length fatty acids glycerides are present. Changes in the GLC profiles before and after the reaction indicate the changes in the glyceride composition. Palm kernel oil (26) was examined before and after interesterification(Table VI).Composition of the interesterified oil agrees closely with that calculated for random distribution. This method is fast (20-30 min) and generally yields good results with fats or mixtures containing fatty acids of different chain length and high in saturated fatty acids.

Mass Spectrometry

This method provides a molecular weight distribution of triglycerides mixtures. Analysis of natural and randomized cocoa butter are shown in Fig. 9. Randomization produces the greatest change on the disaturated glycerides POS and SOS, which are reduced significantly. This method is also fast and has been applied to such highly unsaturated oils (32) as corn, soybean, sunflower and safflower.

Pancreatic Lipase Hydrolysis

Pancreatic lipase specifically hydrolyses the fatty acids attached to the primary hydroxyl group of glycerol and produces 2-monoglyceries from triglycerides. The fatty acid composition of these 2-monoglycerides reveals the specific distribution at the 2-position of the glyceride. If the fat has a random distribution of fatty acids, then the distribution at the 2-position will be the same as for the total fat. Thus the 2-monoglyceride obtained by pancreatic lipase hydrolysis will have the same composition as the total fat. Results of lipase hydrolysis for lard and randomized lard (33) are presented in Table VII.

The fatty acid composition of lard is distinctly different from that for the 2-position. The 2-position is taken predominantly by 16 carbon acids, mostly palmitic. On randomization, the composition of the randomized fat and that for the 2-position are identical. This is the most conclusive proof for the random distribution of fatty acids due to interesterification. This was confirmed for corandomized

TABLE III

Changes in Sci Values Due to Interesterification (17,21,22,23,24,25,26)

	Before			After		
	10 C	20 C	35 C	10 C	20 C	35 C
Cocoa butter	84.8	80	0	52.0	46	35.5
Palm oil	54	32	7.5	52.5	39	21.5
Palm kernel oil	---	38.2	8.0	---	27.2	1.0
Hydrog. palm kernel oil	74.2	67.0	15.4	65	49.7	1.4
Lard	26.7	19.8	2.5	24.8	11.8	4.8
Tallow	58.0	51.6	26.7	57.1	50.0	26.7
60% palm oil – 40% coconut oil	30.0	9.0	4.7	33.2	13.1	0.6
50% palm oil – 50% coconut oil	33.2	7.5	2.8	34.4	12.0	0
40% palm oil – 60% coconut oil	37.0	6.1	2.4	35.5	10.7	0
20% Palm stearine 80% Lightly hydrog. vegetable oil	24.4	20.8	12.3	21.2	12.2	1.5

TABLE IV

Change in the Ratio of $SU_2/S_2U = R_1$ During Interesterification (29)

Glyceride Temp. Catalyst	POP 100 C Sodium ethoxide t(min)	R_1	POS 120 C Sodium t(min)	R_1
	2	0.03	5	0.01
	5	0.14	7	0.03
	10	0.21	10	0.18
	20	0.29	15	0.40
	30	0.37	20	0.47
	60	0.50	30	0.49
			45	0.50
			60	0.50

TABLE V

Selected Glyceride Changes during the Corandomization 60% Sunflower Oil and 40% Fully Hydrogenated Lard (30) 0.2% NaOMe 70-90 C[a]

Triglyceride group	No. of double bonds	Minutes after start			33.	
		0[b] (%)	20 (%)	40 (%)	60 (%)	Difference[c]
S_3	0	37.7	32.0	17.1	6.1	-31.6
S_2O	1	---	0.7	3.7	9.2	+ 9.2
S_2L	2	0.5	2.9	12.7	20.9	+20.4
SOL	3	4.7	5.2	11.2	14.0	+ 9.3
SL_2	4	11.4	11.8	16.2	20.2	+ 8.8
OL_2	5	20.3	20.2	16.5	9.5	-10.8
LLL	6	19.2	19.4	14.3	11.6	- 7.6

[a] S—saturated, O—oleic, L—linoleic.

[b] Composition of starting mixture.

[c] Difference between randomized (60 min.) and starting mixture.

mixtures of soybean oil and soybean stearine (34). Besides these, other methods such as cooling curves (19,22), differential scanning calorimetry (26) and x-ray diffraction (35,36,38) have been used to detect changes effected by interesterification. In summary it may be pointed out that efforts to speed up solids content determination (pulsed NMR) and glyceride composition (argumentation TLC) would be greatly helpful.

INDUSTRIAL PRACTICE

Interesterification involves three important steps, pretreatment of oil, reaction with the catalyst and deactivation of the catalyst. Poisons that consume the catalyst or inactivate the active catalyst once it is formed include moisture, free fatty acids and peroxides. The amount of catalyst such as sodium methoxide and sodium hydroxide required to counteract these poisons are given in Table VIII. Of these, moisture deactivates the highest amount of such catalysts as sodium and sodium methoxide, and thus with these catalysts, drying of the oil is an important step. Freshly refined oil will have low acidity, and any heating of the oil at high temperatures (120-150 C) under vacuum such as during drying usually reduces the peroxide content.

Batch Process

A reactor, provided with an agitator, heating and cooling, nitrogen sparging and vacuum such as one shown in Fig. 10, is usually employed. The fat is heated under vacuum with nitrogen sparging until dry. After cooling to the reaction temperature, the catalyst is sucked in and the interesterification is performed for the desired period. The reacted mixture is pumped into a refining vessel and sprayed with water to deactivate the catalyst. The rest of the treatment is similar to refining.

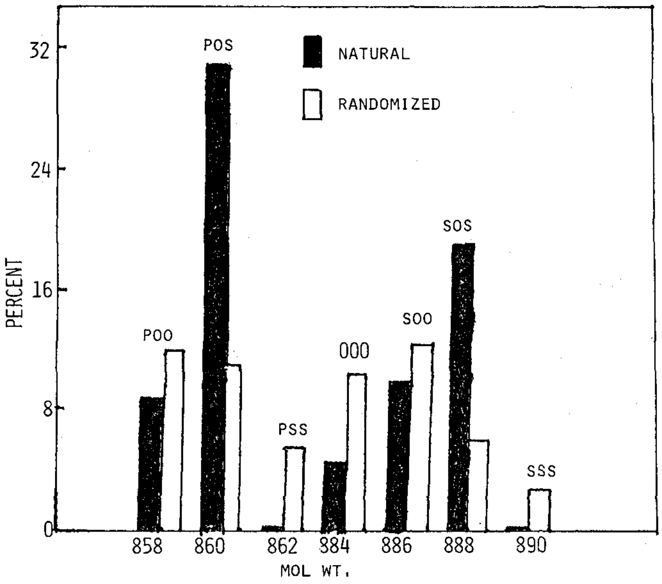


FIG. 9. Partial glyceride composition of natural and randomized cocoa butter by mass spectrometry (32).

Continuous Process

The flow diagram for a continuous process with sodium as catalyst is shown in Fig. 11. The heated oil is dried under vacuum by flashing, which brings the moisture level to about 0.01%. Sodium is introducted into the hot oil in the form of a fine ribbon and is melted almost immediately. The catalyst oil mixture is homogenized to disperse the catalyst. This homogenized mixture is passed through a

TABLE VI

Partial List of Triglyceride Carbon No. Analyses by GLC 26

Triglyceride carbon no.	Palm kernel oil (PKO)	Interesterified^{a} PKO	Calc'd. for random distribution
36	21.1	16.4	16.8
38	16.2	16.2	14.7
40	9.6	12.7	14.9
42	9.2	18.6	19.3
44	6.8	10.4	10.5
46	5.5	5.8	6.7

^{a}0.4% NaOMe, 100 C, 15 min.

TABLE VII

Pancreatic/Lipase Hydrolysis of Lard and Randomized Lard 33

	Lard		Randomized lard^{a}	
Fatty acid	Total fat	2-Position	Total fat	2-Position
16:0	24.8	63.6	23.8	24.2
16:1	3.1	6.4	2.9	3.3
18:0	12.6	3.0	12.2	12.0
18:1	45.0	16.5	47.2	47.4
18:2	9.8	5.1	9.5	9.8
Other acids	4.7	5.4	4.4	3.3

^{a}0.3% NaOMe, 90-100 C, 2 hrs.

TABLE VIII

Inactivation of Catalysts by Poisons

Poison		Catalyst inactivated lbs./1000 lbs. of oil		
Type	Level	Sodium	Sodium methoxide	Sodium hydroxide
Water	0.01%	0.13	0.3	- - -
Fatty acid	A.V.=0.1	0.04	0.1	0.07
Peroxide	P.V.=1.0	0.023	0.054	0.04
Total catalyst inactivated		0.193 lb.	0.454 lb.	0.11 lb.

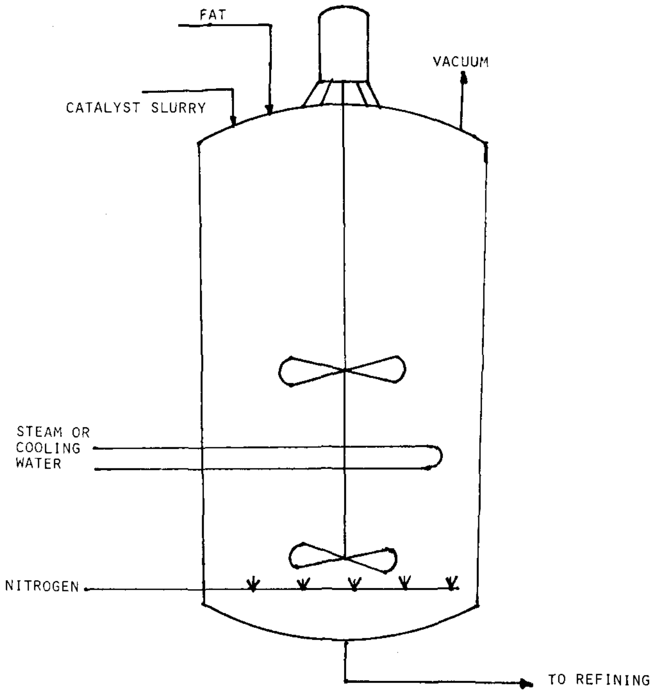


FIG. 10. Batch reactor for interesterification.

tubular reactor. The residence time in this reactor determines the period of the reaction and therefore is adjustable by changing the coil length. The catalyst is deactivated with water in a mixer. The soap and oil are separated by a centrifuge. If washing of the oil is desired, an additional washing centrifuge can be installed at this stage. The washed oil is dried.

APPLICATIONS

Since random interesterification changes the melting and crystallization characteristics, it finds applications in such fields as shortenings, margarines and confectionary fats where these characteristics are important. Numerous patents describe these applications and a few will be discussed.

Shortenings

Lard (19,22,24,35,36) is the most investigated fat for this purpose. Lard produces very coarse crystals, and this is attributed to the presence of a high proportion of palmitic acid in the 2-position of its disaturated (S_2U) glycerides (33,37). On randomizing, the proportion of palmitic acid in the 2-position is reduced from about 64% to 24% - Table VII. Concurrently other glyceride changes also occur, and these produce a smooth textured lard. Natural lard tends to crystallize in the β-phase (36) (4.6A°), while randomized lard crystallizes in the β^1 (4.2A°) (38), phase. Randomization of lard improves its plastic range and thus makes it a better shortening than natural lard.

Margarines — High Stability Margarine Blends

Presence of long chain fatty acids (20 to 22 'C' atoms) provides stiffening power, and the presence of short chain acids (6-14 'C' atoms) on the same glycerides produces better melting qualities. Both these properties can be com-

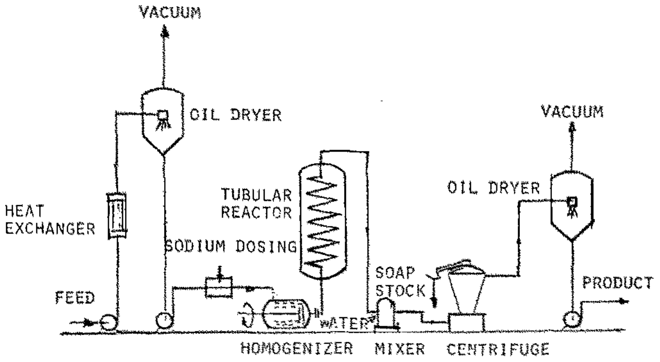


FIG. 11. Continuous interesterification with sodium as catalyst.

bined by using randomized oils(39): 75 parts (corandomized 40% coconut oil/60% palm oil), 10 parts (corandomized 50% coconut oil/50% hydrogenated rapeseed oil IV 4) and 15 parts hydrogenated soybean oil IV 95. SCI of the blend at 10 C, 10 C, 33.3 C are 32, 19, 3.1 respectively. Margarine made from this blend has good spreadability, high temperature stability and good eating qualities.

Nutritional Margarine Blends

High polyunsaturated content and low to zero trans acid containing margarines are produced by interesterifying a blend of liquid oil and a fully hydrogenated oil, e.g., 75 parts soybean oil plus 25 parts fully hydrogenated cottonseed oil interesterified with sodium methoxide (40). The product has the following characteristics: M.P. 39 C (102-4 F); essential fatty acids 44.6; trans acid 2%. Similar formulations using an interesterfied blend of soybean oil and soybean stearine has been reported recently (34). For a randomized blend of 80 soybean oil/20 soy stearine, SCI values 10, 21.1, 33.3 C are 8, 3.4 and 2.2 and the polyunsaturated content (18:2 + 18:3) 51.5% and trans content 1.6%. Flavor and oxidative stability of the margarines made from interesterified oils were observed to be good.

Confectionary Fats

Due to the high price of cocoa butter, a number of substitutes have been developed using interesterification of lauric fats with other fats. Hydrogenated palm kernel oil is a hard butter melting at 46 C and produces a waxy feel in the mouth. On randomization its melting point is reduced to 35 C. By blending hydrogenated palm kernel oil and its randomized product, a whole series of hard butters with highly desirable melting (rapid melt in mouth) qualities are obtained. Some of these blends are listed in Table IX. The big drop in the solids content between 20 C and 38 C (mouth temperature) is responsible for the rapid melt in the mouth.

Partial or fully hydrogenated lauric fats are corandomized with such non-lauric fats as fully hardened cottonseed (41,43) oil or long chain acid containing oil as fully hydrogenated rapseed, herring etc. oil (42). Such corandomized fats have better gloss-producing and quick set-up properties.

DIRECTED INTERESTERIFICATION

It was observed earlier, Fig. 1, that interesterification tends to produce an equilibrium composition of triglycerides. If such a reaction mixture is cooled to below its melting point, the trisaturated glycerides will start crystallizing out. This selective crystallization upsets the equilibrium, and the reaction will commence again to produce more trisaturated glycerides to re-establish equilibrium. Theoretically this process will continue until all the saturated fatty acids are converted into trisaturated glycerides (12). Since this reaction is directed toward the path to produce a particular type of glyceride, it is referred to (11) as directed interesterification. This reaction depends on the directing influence exerted by crystallization. The composition of the final directed mixture starting with SOL would be:

Stearic-stearic stearic	33.33 mol %	Solids
Oleic-oleic-oleic	8.33 mol %	Liquid
Linoleic-linoleic-linoleic	8.33 mol %	
Oleic oleic linoleic	24.99 mol %	
Oleic linoleic linoleic	24.99 mol %	

The changes in solids content due to directed interesterification are demonstrated in the case of lard, Fig. 12. Crude lard has low solids content at warm temperatures. Randomization improves crystallization at low temperatures but needs addition of stearine for high temperature stability. Directed interesterification produces a lard with increased solid content at high temperatures and thus an extended plastic range. Therefore, directedlard can be used as a shortening without any addition of fully saturated glycerides.

A flow diagram for directed interesterification of lard using NAK alloy as catalyst is shown in Fig. 13. Freshly refined lard was dried to a moisture content of 0.01% and then cooled to 104-108 F (40-42 C). It was pumped into a mixer where the NAK catalyst is metered in and the lard-catalyst mix passes through a coil (hold time 15 min) for radomization to occur. The randomized mixture is cooled to 68-71 F (20-22 C) by pumping through a votator (ammonia cooled) with a residence time in the votator of 0.5 min. The crystallized mass passes into a picker box in which the mixture is agitated for an average time of 2½ min. Due to the heat of crystallization the temperature rises to 81-83 F (27-28 C). It is again cooled down to 70 F by passage through another ammonia cooled votator. From here the mixture is pumped through a series of crystallizers with gentle agitation and a holding time of 1½ hrs. The stock leaving the crystallizer is at a temperature of 86-90 F (30-32 C) and is treated with CO_2 and water in a high speed mixer to kill the catalyst. The soap that forms is removed by centrifugation and the lard washed further till free from soap. The washed lard is dried. The final control is SCI at 92 F which should be about 14.

In recent years, palm oil has become available in large quantities commercially. Directed interesterification and fractionation has been applied(48) to palm oil to produce a

TABLE IX

Confectionary Fats from Blend of Hydrogenated and Interesterified Hydrogenated Palm Kernel Oil

		SCI			
Fat	M.P. C	10	20	35	38
Hydrog. palm kernel oil (PKO)	46.8	74.2	67.0	15.4	11.7
Int. hydrog. PKO	35.0	65.0	49.9	1.4	1.1
50% Hydrog.:50% int. hydrog.	41.7	70.0	57.4	8.7	5.2
65% Hydrog.:35% int. hydrog.	44.2	71.0	59.7	10.2	6.7
80% Hydrog.:20% int. hydrog.	46.0	72.4	62.6	12.4	8.5

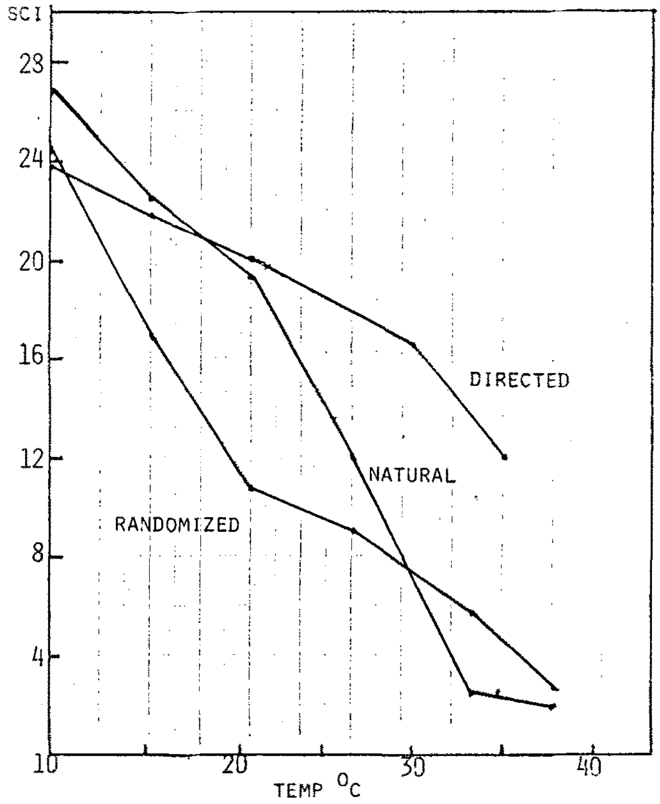


FIG. 12. Changes in the sci of lard due to rearrangement.

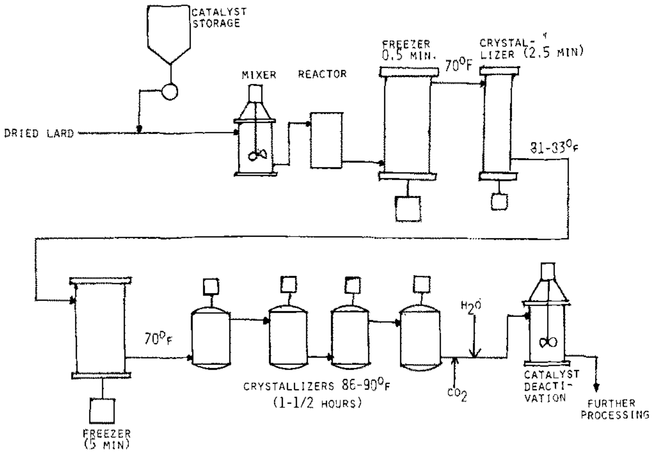


FIG. 13. Directed interesterification of lard.

salad oil. The solid content of palm oil, randomized palm oil and directed interesterified palm oil are shown in Figure 14. Randomization produces only small changes in the solids content of palm oil, but directed interesterification increases the solids at higher temperatures significantly. Fractional crystallization of palm oil at 20 C produces a liquid fraction with a cloud point of 5 C. Fractionation after directed interesterification results in a liquid fraction with a cloud point of 2.7 C, and thus a better salad oil is obtained.

Interesterification and directed interesterification were observed to proceed at an accelerated pace in the presence of catalyst activating solvent such as dimethyl sulfoxide (44). Thus cottonseed oil directed interesterified at 0 C for one day had a SCI of 11.4, and this rose to 18.0 if the reaction was performed in the presence of 1% dimethyl sulfoxide. The practical application of this process is the directed interesterification of sunflower and safflower oils at -10 C in the presence of 1% dimethyl sulfoxide to produce stocks suitable for margarine (45). Safflower oil directed interesterified this way had SFI of 4.2 at 0, 4.3 at 21.1 C 2.8 at 33.3 C and 0 at 40 C. Sunflower oil similarly directed interesterified had SFI's of 10.7, 6.0, 5.2 and 2.1 at 0, 21.1, 33.3 and 40 C, respectively. Margarines made from both these directed oils had acceptable properties.

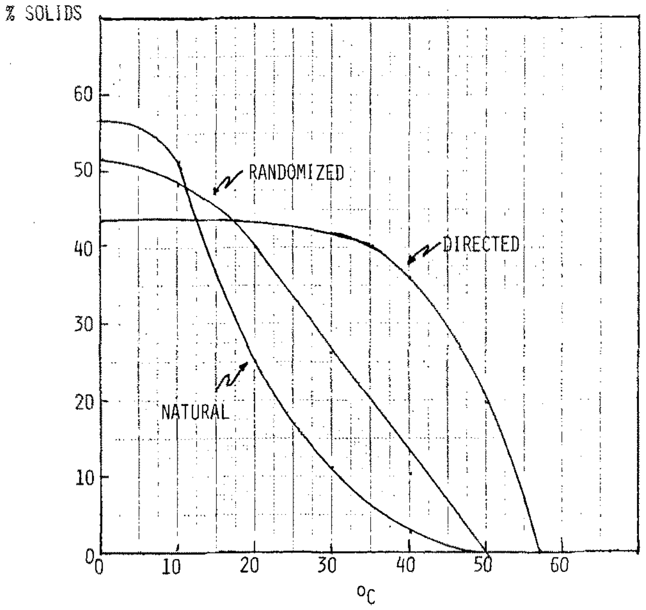


FIG. 14. Solid contents changes in palm oil due to random and directed interesterification.

Another method of accelerating the reaction is by cycling the temperature of the reaction mixture between 1-15 below and to at least 5 above its cloud point (45). Thus sunflower oil, interesterified with 0.25% Na, was cycled between -5 C and 10 C for 24 hours to yield a product having higher solids content than a control sample chilled first to -5 C for 0.5 hour and then held at 10 C for 47.5 hrs.

A process using selective extraction (47) of glycerides to upset the equilibrium and thus induce directed interesterification has been reported. An advantage of this process is that fractions lean in a particular fatty acid can be obtained. Interesterified soybean oil dissolved in heptane is contacted in a column with a counter current flow of dimethyl formamide. A partitioning of the glycerides according to their unsaturation occurs between the solvents. The dimethyl formamide picks up the more unsaturated glycerides. In a typical experiment a fraction containing about half the linolenic acid of the parent oil but substantially retaining all of the linoleic acid is abtained.

	Linoleic	Linolenic
Original oil	48.0	6.8
Treated oil	47.0	3.0

The selected applications described above demonstrated the importance of interesterification and directed interesterification as processing tools.

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