Directed Interesterification as a New Processing Tool for Lard

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For many years lard has been one of the chief food fats produced in the United States, constituting about 30% of the total food fat supply here. This situation is likely to continue, considering the growing production of meat and the corn-hog economy in this country. Prior to the development of the hydrogenated vegetable oil shortening, lard was also the premium shortening here and enjoyed a substantial price advantage over the cheaper "lard substitutes" of the day. However, in the past 30 years or so, the hydrogenated vegetable shortenings have gradually supplanted lard as the "quality" product in the average consumer's mind. Evidence for this is in the average price of lard to the consumer, relative to vegetable shortening. Lard once sold at a substantially higher price than vegetable shortenings; it now sells on the average, substantially under (1). This economic pressure has stimulated research into ways of increasing the consumer acceptance of lard.

When compared to the good hydrogenated vegetable shortenings, "natural" lard has:

a) a poor oxidative stability, creating off-flavor problems in storage and in high temperature uses such as frying and pastry;
b) a grainy, translucent appearance and texture that is unattractive compared to the smooth, white appearance of vegetable shortenings and causes performance difficulties in some baking uses;
c) a poor plastic range, that is, it usually is too soft at warm temperatures and too hard at cold temperatures; and
d) non-uniformity in consistency and flavor, which can vary with the season, area, and rendering method.

Great improvement has been made in the oxidative stability by the use of the approved antioxidants (2) although, for frying performance equal to the better vegetable shortenings, it appears that the lard should be hydrogenated as well as treated with antioxidants. The use of antioxidants in lard is now widespread in this country. Random interesterification of lard can cure the graininess problem in lard (3) and has been in use commercially in the past few years (4, 5, 6). In randomization the fatty acids regroup as new triglycerides according to the laws of chance. It is thought now that the grains in natural lard are nearly pure crystals of disaturated glycerides which, in natural lard, are largely UPS (U = unsaturated, P = palmitic, S = stearic) (7). Probability calculations show that if the 26% or so of disaturated glycerides in natural lard were all UPS, then after randomization only about 3.4% of this particular variety would remain.[1]

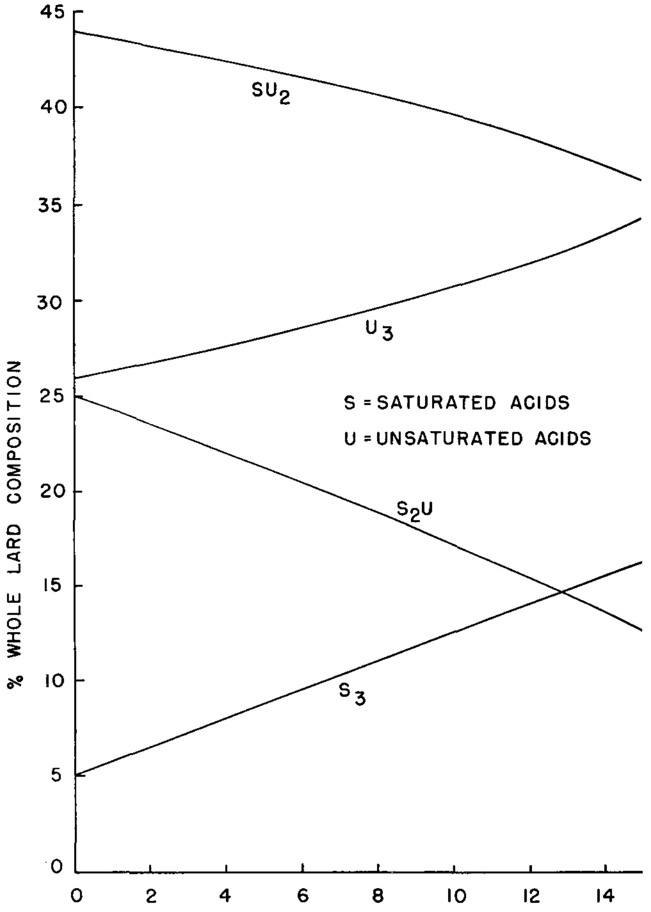

FIG. 1. Calculated change in lard glyceride composition with directed interesterification.

Even after randomization, however, the plastic range problem remains, for most of the solids in lard or randomized lard are disaturated glycerides, which give little or no heat resistance to the shortening since they melt in the room temperature range. Thus, it is customary to add some 9–12% of completely hydrogenated fat (usually cottonseed oil) to the randomized fat to impart sufficient body or plasticity at the warm temperatures. This method is not only costly but creates the problem of the shortening now being perhaps too firm at cold temperatures. This hardness at temperatures below room temperature also limits the amount of hydrogenation that can be done to the lard to improve its frying performance, since hydrogenation adds "intermediate" melting solids which make the lard still firmer at temperatures of 70°F. and below. The solution to this problem of plastic range, the last important weakness in lard, lies in directed interesterification (9, 10). The development of a practical and economical plant process for directed interesterification and the successful factory application of it are the subjects of this paper.

Chemistry of Directed Interesterification

In directed as contrasted to random interesterification, the reaction is carried on just below the melting

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[1] A typical lard contains 27% palmitic acid, 10% stearic acid, and the remainder unsaturated or "liquid acids" (51% oleic, 11% linoleic, 0.6% linolenic, 0.4% arachidonic acids). The probability of triglycerides occurring containing one each of U, P, and S in a completely random distribution in lard would be: $(.27 \times .10 \times .63)\ 6 = .102$. However the probability that P will occur in the β or 2 position, as UPS, is $\frac{1}{3}$ of $.102 = .034 = 3.4\%$ (8).

point of the fat so that the highest melting fractions, the trisaturated glycerides, are made to precipitate, thus leaving the liquid phase where interesterifying takes place. This forces the equilibrium in the direction of formation of more trisaturated glycerides which in turn can precipitate, etc.

The progress of this type of interesterification can best be illustrated by plotting the course of the several glyceride types against the percentage of trisaturated glycerides that precipitate (Figure 1). These curves are calculated curves, assuming that the liquid phase during the directed interesterification is always "random."[2] As the fraction of trisaturated glycerides in lard is increased by directed interesterification, the disaturated and monosaturated glyceride fractions must decrease. The following are suggested by these curves.

a) The trisaturated glycerides formed by directed interesterification could eliminate the need for addition of completely hydrogenated fat (hardstock) to lard, as is now customary to provide necessary heat resistance.

b) The decrease in disaturated glycerides of directed interesterified lard should mean less total solid glycerides at cold temperatures (50°F.) than would be present in natural or random interesterified lard to which the customary 10% or so of "hardstock" has been added.

c) If no "hardstock" needs to be added to directed interesterified lard, then it would be expected that more hydrogenation could be performed on this lard for any given hardness or penetration level than could be performed on random interesterified lard to which the customary amount of hardstock has been added.

d) Because the disaturates are reduced some 25–30%, the 2-palmityl oleyl stearin (UPS) will also be reduced correspondingly, causing a theoretically greater resistance to graining of disaturated glycerides in the shortening than in random interesterified lard.

In the work on interesterification it was necessary to find analyses that specifically indicated, or could be correlated to, the percentage of trisaturated glycerides present. The tests found most useful were cloud-point and the dilatometric behavior of the fat at various temperatures. The cloud-point is the temperature at which a definite cloud forms when the liquid fat is cooled at a definite rate. Figure 2 shows that it correlates very well with trisaturated content as determined by conventional fractional crystallization procedures (11). The cloud-point can be determined in a few minutes so is ideal for a factory control test. The dilatometric behavior of fat, though a longer procedure, is much more informative since it gives an estimate of the fraction of solids present in the fat at any temperature or after any particular time-temperature history. The dilatometric method used in this work (12) is referred to as the solid content index (SCI) method since the percentages of solids are estimates only. However they are very close to the real values. Figure 2 also shows the correlation between percentage of trisaturates and SCI determined at 92°F. for directed interesterified lards.

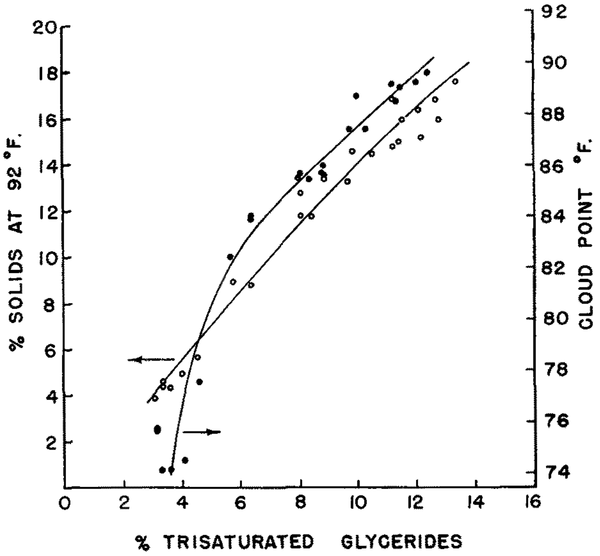

FIG. 2. SCI and cloud-point as control tests for trisaturated glycerides in directed lard.

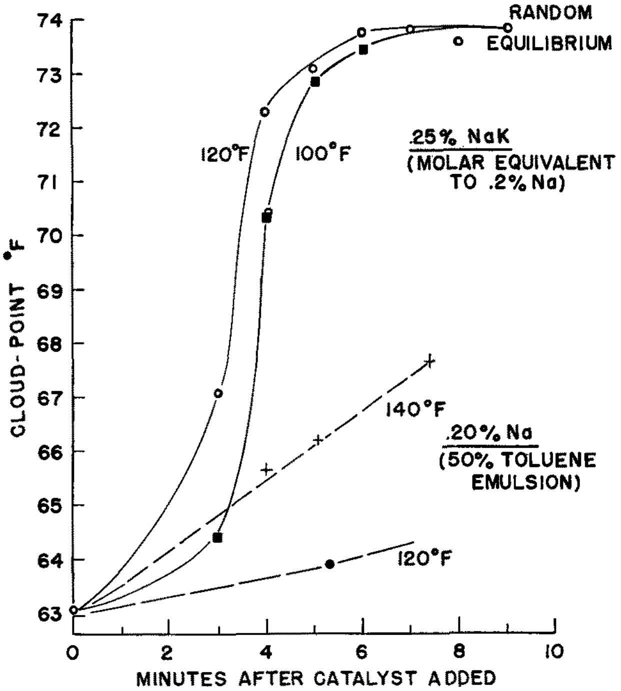

FIG. 3. Effect of temperature and catalyst-type on rate of random interesterification.

Pilot Plant Development

Initially the laboratory work and preliminary pilot plant work were done batchwise. The usual method of operation was to mix the catalyst (sodium methoxide or sodium) in the melted and previously dried fat, then gradually cool the mass of fat by setting the batch at successively lower temperatures or by circulating cooling water through coils or a jacket. Slow agitation was used to aid heat transfer. When the trisaturated glycerides began to crystallize, the viscosity of the mass increased sharply, the heat transfer became poor, and agitation became difficult. The reactions under these conditions usually took anywhere from several hours to several days to reach the desired quantities of trisaturated glycerides.

When considering factory-scale equipment for large productions of directed interesterified lard, it became clear that the batch process would be clumsy, difficult

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[2] In actual practice, equilibrium in the liquid phase is probably never achieved during directing since the trisaturated glycerides will tend to precipitate as soon as they are formed by interesterification. Their low solubility at directing temperatures (80–100°F.) precludes amounts in the liquid phase as high as indicated on the curve. However the curves do illustrate accurately the relative trends and amounts of the four classes of triglycerides.

to control, and expensive because of the many tanks that would be needed. It appeared that a practical answer might be in a continuous process where only relatively small amounts of material are being treated at any one instant.

In analyzing the factors that control or limit the rate of directed interesterification, it became apparent that the following four are most important:

a) rate of interesterification in the liquid phase (randomization);

b) rate of heat removal;

c) extent of nucleation, *i.e.*, number of crystal centers formed on which trisaturates can crystallize; and

d) rate at which the trisaturates crystallize out of the liquid phase.

The rate of random interesterification is important since the trisaturated glycerides can only precipitate as fast as they are formed in the liquid phase. As shown in Figure 3, the rate of randomization can be relatively rapid when a very active catalyst is used, such as sodium-potassium alloy (NaK). Cloud-point is used in this case to indicate where equilibrium is reached, which for this lard sample was 73.9°F. NaK (liquidus curve shown in Figure 4 for reference) is a liquid under normal room temperatures, and this property makes it well suited for continuous metering. The greater activity of NaK (over sodium alone) can probably be explained also by its liquid properties. The surfaces of the catalyst particles in fat undoubtedly become coated with oxide by reaction with traces of oxygen and peroxides in the fat. The sodium particles, being solid, are partially blocked by this oxide coating whereas the NaK particles, being liquid, apparently keep unreacted metal on the surface. This can be observed in another manner. Small particles of NaK in air will catch fire from rapid oxidation whereas similar sodium particles will usually oxidize on the surface only.

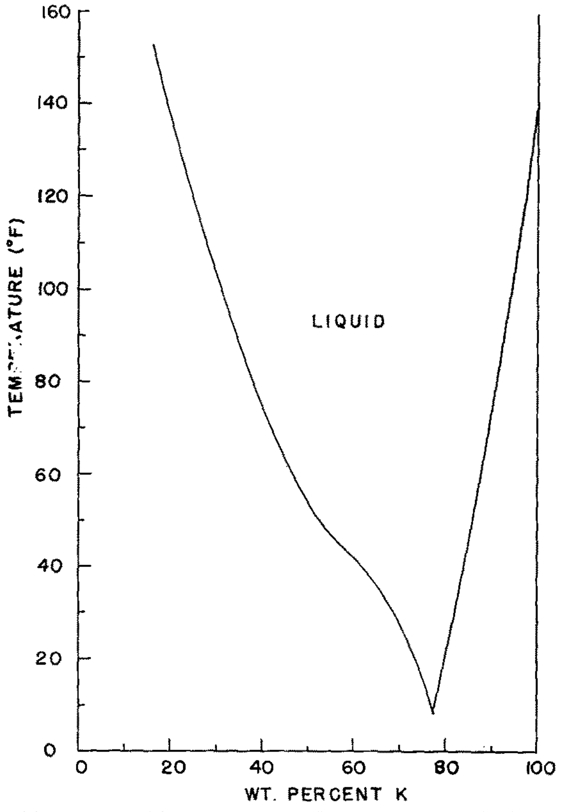

FIG. 4. Liquidus curve for sodium-potassium (13).

Heat removal from fat, especially a mixture of solid and liquid fat, is difficult because of the poor conductivity of the fat and the relatively low convection obtained in such a viscous or plastic medium. The heat to be removed totals about 28 BTU/lb. fat, of which part is sensible and the remainder is heat of crystallization. High heat removal rates were obtained by using commercial Votator units, which are scraped-wall heat exchangers used commonly in shortening manufacture. Heat transfer rates of about 250 BTU/(hr.) (sq. ft.) (°F.) were obtained with this equipment.

The problem of forming many nuclei or crystal centers was also solved with the Votator chilling equipment for the fat is chilled so fast (15 seconds) to a temperature well below its melting point that a fine cloud develops quickly, consisting of many more nuclei than would be obtained with a slow chilling process.

After the interesterifying liquid lard is chilled to a low temperature and nucleation accomplished, there still remains the crystallization of the trisaturated molecules. This is probably the limiting factor in the process as it now stands. The crystallization of trisaturated glycerides is a diffusional process and is greatly hindered by the very viscous nature of the lard at this stage. Agitation is of considerable aid in accelerating crystallization, and a study was made of agitation as applied to this problem. The optimum agitation appears to be a gentle but thorough movement throughout the crystallizing mass. Too little agitation results in partial solidification of the crystallizing lard, and too much results in excessive heat input.

As finally developed in the pilot plant, the process is essentially as follows. Prime steam (or dry rendered) lard is pumped first through a vacuum drying step, and then cooled to a temperature just above its melting point by passage through a heat exchanger. A carefully metered stream of catalyst (NaK) is then pumped with the lard into a small continuous mixer, where the NaK is suspended throughout the lard as particles, 10–40 microns in diameter. The catalyzed lard continues on through a brine-cooled, scraped-wall heat exchanger, in which the temperature is quickly dropped to the point desired for initiating crystallization of trisaturated glycerides. Stock leaving the cooler goes to an agitated vessel, where the directed interesterification proceeds under carefully controlled agitation. Two things are happening simultaneously: any trisaturated glycerides present will start to crystallize; and interesterification in the liquid phase will form more trisaturated glycerides to try to restore the equilibrium distribution. This initial crystallization of trisaturated glycerides liberates considerable heat of fusion, which takes the temperature up beyond the desired range, and a second cooling step is required to bring the stock back down to the desired temprature. After the second cooling the lard passes to a second crystallizer, where the precipitation of trisaturated glycerides continues to whatever level is desired. The crystallization slows down as the driving force diminishes so that the second crystallizing stage is larger to allow more time for completion of the reaction. The end-point is determined by either

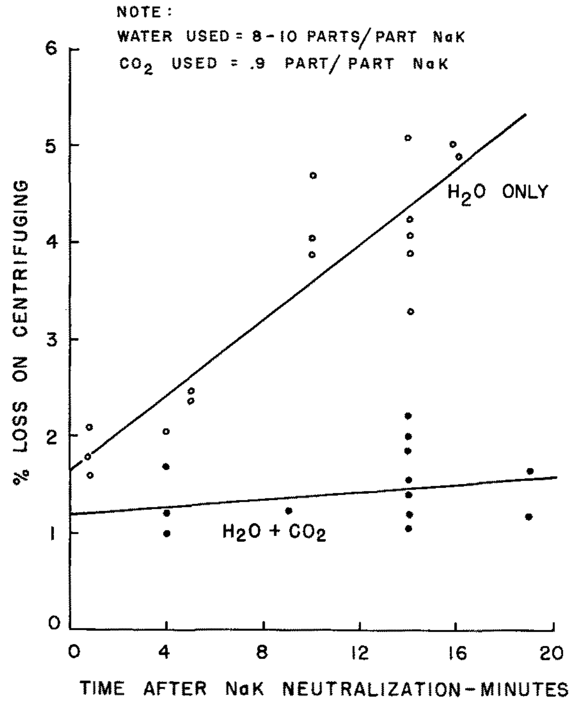

FIG. 5. Effect of time and neutralizing reagent on "refining" loss in directed lard.

a cloud-point or a solid content index measurement of the stock leaving the crystallizer. The level of trisaturated glyceride formation can be changed by varying the time in the crystallizer or varying the temperature at which crystallization is taking place, or a combination of both.

When the directed interesterification has reached the desired point, the catalyst is "killed" by adding water. The amount of water is calculated to give the proper fluidity to the soap phase for refining, the next step. Since the amount of caustic formed by simple "killing" of the catalyst with water would result in high refining losses (by saponifying neutral lard), CO_2 is injected with the water. CO_2 buffers the caustic to a lower pH and minimizes saponification of the lard, especially if there is an appreciable time lag between "killing" the catalyst and separating the soap (Figure 5). The neutralized lard must now be heated to melt the trisaturated glyceride crystals so that the soap phase may be separated from the lard in a conventional centrifuging operation. This interesterified and refined lard is now ready for further processing to a finished shortening. A basic flow chart for the directing process is given in Figure 6. The exact processing conditions, of course, vary, depending on the crude lard firmness and the amount of trisaturated glycerides desired in the finished product. Patent applications are pending on the various aspects of this process.

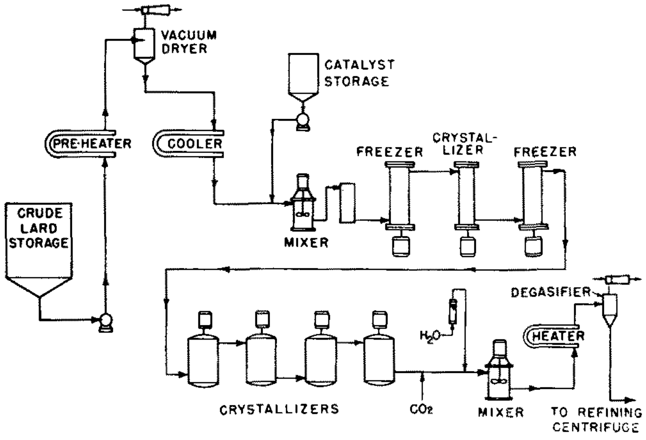

FIG. 6. Basic flow chart for directed interesterification of lard.

The best way of demonstrating the change made through directed interesterification is by the dilatometric behavior at various temperatures. Figure 7 shows SCI change with temperature for a typical lard that is random interesterified, directed interesterified, and the crude starting lard for comparative purposes. These curves show the lack of solids in the warm temperature range, for the randomized and the "as is" lard, which is the reason for the need to add a high melting fraction to these products to produce a shortening with satisfactory heat resistance. When completely hydrogenated fat ("hardstock") is added, of course, the percentage of solids is increased at all temperatures below the melting point. Figure 7 illustrates that the effect of directed interesterification is to increase the solid fraction at the warm temperatures without any appreciable change in the low temperature range.

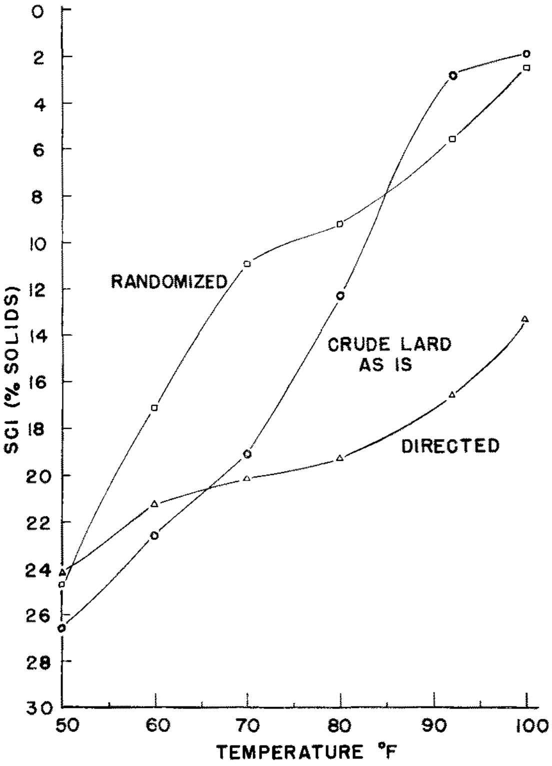

FIG. 7. Effect on the lard SCI *vs.* temperature curve of random and directed interesterification.

Factory Application

A detailed flow chart was prepared, using the basic information obtained from pilot plant work. There were a number of new problems that arose in designing the plant unit concerned with instrumentation, safety, ease of operation, and process control. As an aid in resolving these problems, a complete model of the proposed plant was made, including piping and instrumentation. Using the model for simulating actual plant start-up, shutdown, and operation made it considerably easier to arrive at the optimum arrangement of equipment and instrumentation. Concerning safety, it was attempted to visualize every circumstance where the failure of one instrument, control, or pump might cause a hazardous situation to arise.

The hazards are mostly concentrated in the NaK drum storage area, the unloading of the drums into the NaK scale tank, and the metering of the NaK into the lard stream. All steam or water lines were eliminated from the NaK storage area, and the floor was sloped to the center so that leakage or spills would drain to the center of the room. The NaK drums are unloaded by nitrogen pressure in a separate cubicle where the operator can apply nitrogen pressure (or release it) from outside this area. The NaK scale tanks and metering pumps are adjacent to the NaK storage area and are also enclosed by tile walls.

The metering principle used for the NaK is based upon a variable speed positive displacement pump of special design to prevent valve blockage. The speed of this pump and thus its output are controlled electrically by the speed of a traveling poise on the NaK scale tank. The speed of the traveling poise and thus the speed of the pump can be controlled from the main panel board in the operating area. The entire NaK metering system is interlocked with oil flow so that if the oil flow stops for any reason the system cannot be filled with NaK. Once the NaK is suitably dispersed in the lard, it is safe and constitutes no particular hazard other than a small evolution of hydrogen which must be vented. Once started, the operation of the plant can be monitored and controlled largely from the centralized control panel, which houses motor starters, the NaK metering system controls, the temperature controls throughout the system, the oil flow controls, and the alarm system.

The freezing of the lard-NaK dispersion is done with commercial Votator units, chilled with direct expansion ammonia. Since a freeze-up in this equipment due to a power failure can shut down the plant for several hours, the ammonia system is equipped with controls automatically to "dump" the ammonia if the temperature of the lard falls below a predetermined point.

Considerable study was given to the design of the crystallizers, the most critical part of the process, where the precipitation of the trisaturated glycerides takes place. It had been established in pilot plant work that any substantial end-for-end mixing had to be eliminated as the stock moved through the crystallizer. This was accomplished most practically in the factory by making four stages of crystallization, each stage being a separately agitated vessel for simplicity in design. To avoid pressure vessels, necessary if the system were held hydraulically full, the crystallizers were built so that the lard would overflow by gravity through the four tanks. If the crystallizing lard is kept in gentle motion throughout the mass, it is quite fluid but it will set up hard in any unagitated spot or on any surface not scraped. The agitation principle finally decided upon, after considering many different possibilities, was slowly moving vertical pitched blades which intermeshed with vertical, pitched stator blades. The outside blade moves very close to the vessel wall, keeping it nearly free of solidified lard, and a stator blade likewise cleans the central drive shaft. The time in the crystallizers can be controlled by by-passing one or more vessels and/or varying the level in the last crystallizer. Figure 8 is a photograph of one crystallizer stage and illustrates the principle of agitation used and the plastic nature of the directing lard.

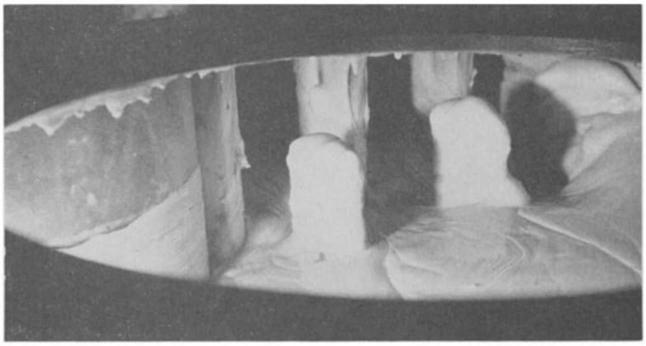

FIG. 8. Inside view of one lard crystallizer during directed interesterification.

The temperature of the lard rises throughout crystallizing due mostly to the heat of crystallization of the trisaturated glycerides. The lard emerges from the crystallizers at 90°F.–100°F., depending on how many trisaturated glycerides are to be formed, and is immediately treated in a high speed mixer with CO_2 and water in order to kill the catalyst. If the catalyst is not killed at the finish of crystallizing, before melting the lard, the reaction will "back up." What soap is formed (from initial free fatty acid in the lard largely) is removed by continuous centri-

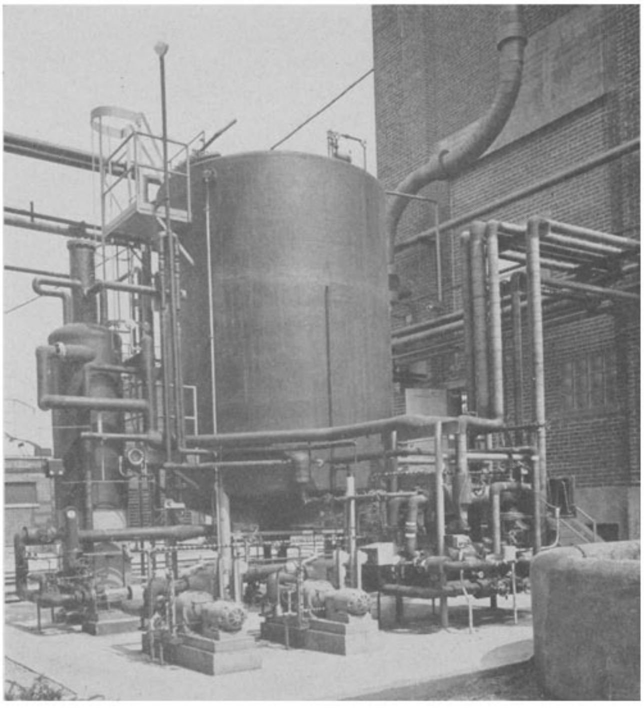

FIG. 9. Outside view of installation showing feed tank, degasifier, and feed pumps.

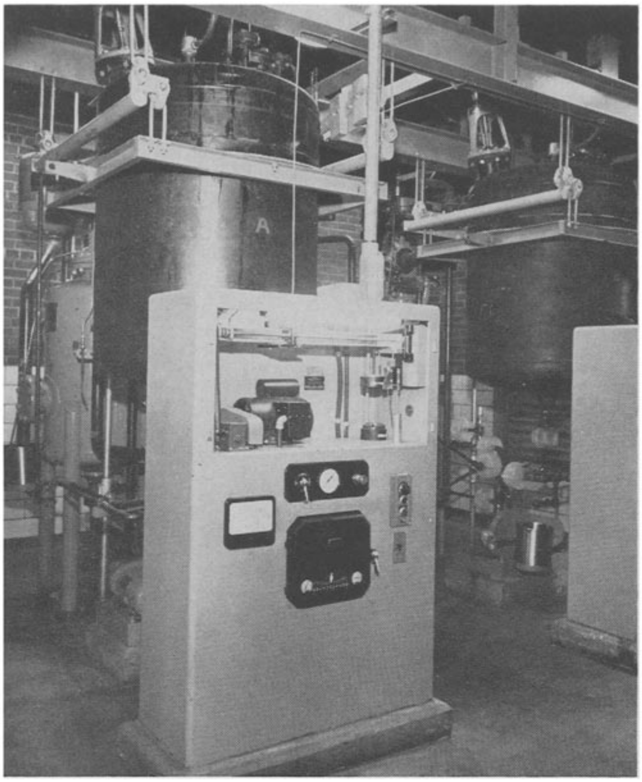

FIG. 10. NaK feed tanks and metering system.

fuges. The residual soaps are further removed by conventional water-washing and centrifuging; and the lard is then dried in a continuous vacuum drier. Controls at this point consist of the usual color and free fatty acid. The final control test for percentage of trisaturated glycerides in the lard is the SCI at 92°F. From this point on, the lard is hydrogenated to the proper point for the desired stability and consistency, deodorized, and plasticized for packaging. Antioxidants and monoglycerides are added after deodorization if desired. General views of one installation are shown in Figures 9, 10, and 11.

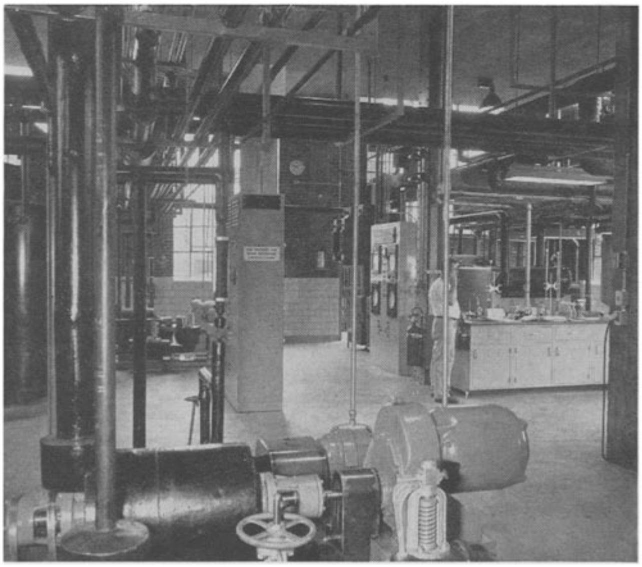

FIG. 11. General view of operating area showing crystallizers (left), Votators (right background), and neutralizing mixer (foreground).

The Product

Both household and bakery shortenings have been manufactured by this process at our Ivorydale and Dallas factories since about January, 1955. The factory production has duplicated the pilot plant product in quality and cost predictions. In overall quality and performance these shortenings have been judged equal to the best vegetable shortenings on the market. The most striking difference, of course, between these directed lard shortenings and the randomized lard shortenings is in plastic range. Figure 12 shows two shortenings, both prepared from the same base lard and both hydrogenated approximately the same amount. The randomized lard has had 9½% of cottonseed oil hydrogenated to saturation added to it to provide heat resistance. Note that the directed lard shortening is softer at temperatures below 70°F. and firmer at temperatures above 70°F. than the randomized lard shortening. As a measure of plastic range, one can take the approximate slope of this line in the middle of the range; or plastic range can be expressed as the number of degrees enclosed between the arbitrary limits of 200 pen. and 300 pen. (the middle of the penetration range). As an example, in Figure 12 the directed lard has a plastic range of approximately 26°F. and the randomized lard, 15°F. Plastic range can be interchanged with oxidative stability in almost all shortenings to some extent in that, by hydrogenating less and adding more "hardstock," the plastic range is improved but the basic or inherent stability is diminished by leaving more polyunsaturated glycerides present. Figure 13 illustrates this interchangeability. The various points shown (open circles) illustrate several different types of commercial shortenings, from the all-hydrogenated "biscuit and cracker" type of shortening with poor plastic range but excellent oxidative stability to the "standard" shortening type with wide plastic range and relatively poor oxidative stability. The solid circles are three different directed lard shortenings of varying degrees of hydrogenation. The plotted line

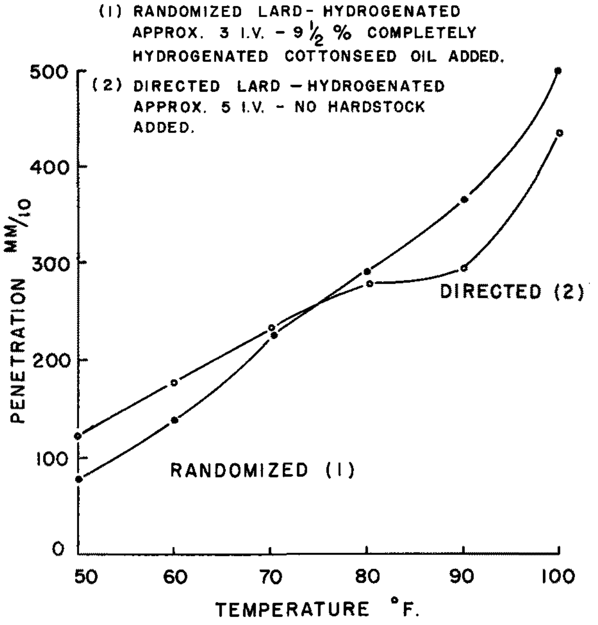

FIG. 12. Penetration vs. temperature curves for random and directed interesterified lard shortenings.

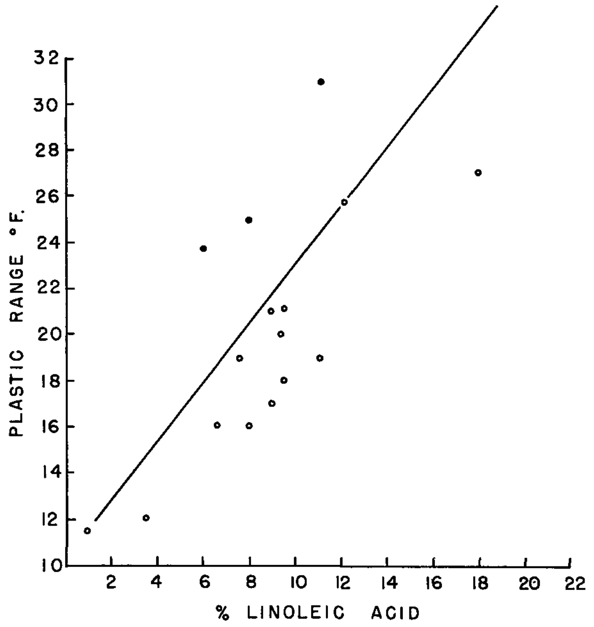

FIG. 13. Relationship between plastic range and % of linoleic acid for all types of shortenings, animal or vegetable (plastic range expressed as °F./100 pen. units, between 300 and 200).

is only intended to estimate the slope or rate of exchange between these two properties and also to separate the areas of conventional shortenings and directed lard shortenings. These data indicate that the directed lard shortenings have better plastic ranges at any given degree of polyunsaturation than any other conventional shortening type.

In baking performance the directed lard shortenings exhibit all of the desirable properties of the premium vegetable shortenings. In addition they also exhibit an improved cake performance at higher batter temperatures, such as would be encountered in the summer in bake shops or kitchens. Another very interesting property of the directed lard shortenings is their stability against change under market-aging conditions. The normal tendency for vegetable shortenings is to firm slightly on aging and become somewhat poorer in texture and blending properties. There is practically no change in the directed rearranged shortenings on market aging in consistency or blending properties. This behavior is possibly associated with the different polymorphic behavior of the solids in vegetable shortenings and those in directed lard shortenings. The former are almost universally in the Beta prime form and stay in this form for years on the market. The fat crystals do grow in size though on aging and tend to intermesh more with a resulting stiffening action. The directed interesterified lard is customarily in the Beta prime form on being freshly made but upon aging slowly changes to the Beta form. It is conceivable that this phase change interrupts the normal tendency of shortening crystals to digest, grow, and become stiffer since it is known that fat solids in the Beta form have less stiffening effect than when in the Beta prime form (14).

Because of the vast flexibility possible with directed interesterification, there has been no difficulty in producing a uniform product out of crude lards that have varied quite widely in hardness.

Summary

The directed interesterification process has been put into successful factory use on lard shortenings. This process increases the fraction of high melting solids (trisaturated glycerides) and decreases the fraction of intermediate melting glycerides (disaturated glycerides) in lard. This change in glyceride composition allows the following advantages to be realized in lard shortenings:

a) an improved plastic range for any given level of oxidative stability, meaning less variation in softness and creaming properties from cold to warm temperatures, achieved without the use of relatively expensive hardstock (completely hydrogenated fat);

b) an improved uniformity from a variable raw material, and a flexibility that makes possible a wider selection of raw materials; and

c) an overall performance equivalent to the premium vegetable shortenings.

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Erratum

A. S. Henick of the Quartermaster Food and Container Institute for the Armed Forces, Chicago, Ill., writes as of December 7, 1955: it has come to our attention that the equation for unsaturated carbonyl in Correction *31,* 447 (1954), contains an error. The denominator of this equation is 0.707, not 0.469 as printed.

The previous correction referred to a paper published on page 88, of the March 1954 issue of the Journal, which was entitled "Estimating Carbonyl Compounds in Rancid Fats and Foods," by A. S. Henick, M. F. Benca, and J. H. Mitchell.