materials, such as sulfur, which increases the amount of *trans* unsaturation.

Although the mechanism of the reaction using sulfur-treated catalysts has not been defined, it appears a sulfur-nickel complex causes the isomerization and any unreacted nickel in the catalyst causes the hydrogenation. Thus, these catalysts are a mixture of 2 catalysts that assist separate reactions.

Looking to the future, one of the great needs in our industry is for a hydrogenation catalyst that will result in hydrogenations of, e.g., dienes and trienes, to monoenes, without formation of any *trans* unsaturation. This would make possible the use of highly unsaturated oils for the production of good flavor, stable salad oils without further processing to remove high-melting glycerides. Thus, in spite of the enormous amount of reach in hydrogenation, there still remain some fundamental problems that need more research.

# Practical Aspects of Hydrogenation and Soybean Salad Oil Manufacture

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## ABSTRACT

Most edible oils are hydrogenated in batch-type slurry converters similar in basic design to those employed when the process was first commercialized in 1911. One major company uses a proprietary continuous slurry process. Other novel batch and continuous slurry systems are available but have not enjoyed significant commercial success. Fixed bed hydrogenation has not been seriously investigated but offers intriguing possibilities. Energy economy is assuming ever greater importance in the design of hardening systems. The accelerated growth of hydrogenation since the 1940s parallels the rapid increase in soybean oil use. In part, it reflects the flavor instability of soybean oil caused by its linolenic ester. When this triunsaturate is lowered by hydrogenation to ca. 3%, a high-quality soybean salad oil can be produced. Standard hydrogenation and separation techniques work well. New separation equipment and processes are entering the marketplace.

Fats have always been a significant part of the human diet, contributing the fuel necessary for energy expenditure. When our ancestors were migrant hunters, their intake of fat was indirect, being consumed as meat and seeds. The rise of agriculture, along with the domestication of animals, resulted in the invention of processes to obtain fats and oils as separate entities. These included the rendering of fat from meat, the pressing of oil from grain or fruit, and the concentration of fats from milk. Obvious examples are lard, olive oil and butter. These processes served the human race well for thousands of years, changing eating habits from opportunity, i.e., "what did we kill or find today," to planned cooking.

The greatly expanding urban population during the Industrial Revolution readied civilization for the invention of a new process that would both improve existing natural fat and oil products and also pave the way for large-quantity production of high-quality, alternate products. That new process was hydrogenation.

Sabatier (1) is usually credited with discovering hydrogenation. His 1897 bench work was quickly picked up by William Normann, who obtained a British patent on liquid-phase hydrogenation in 1903 (2). Procter & Gamble acquired U.S. rights to the Normann patent in 1909 and began marketing Crisco, a vegetable shortening containing hydrogenated fat, in 1911. Note that the time interval from bench discovery through process patent to commercial use was only 14 years and involved 3 entirely disconnected groups in different countries. It is doubtful that we could move as speedily today. Of course, in 1900, there were no government requirements for feeding tests or Environmental Impact Statements, and that certainly shortened the process.

Fortunately for the fats and oils industry, Procter & Gamble's exclusive rights to the hydrogenation process, as spelled out in the Normann patent, were invalidated by the U.S. courts in a short time and the way was cleared for similar shortenings to be manufactured and marketed by others. What sort of products were these? Principally what we, today, call compounds, consisting of either ca. 15% fully hydrogenated cottonseed oil (stearine) blended with refined cottonseed oil, or ca. 10% fully hydrogenated lard added to unhydrogenated lard. Considerable quantities of compounded vegetable shortenings and fortified lard are still consumed in the world today, particularly in less technologically advanced countries.

The next quantum leap in edible oil hydrogenation occurred in the 1930s, when U.S. packaged food processors began the mass marketing of 2 products. One was all-hydrogenated vegetable shortening. This increased the hydrogenated portion of the formulation 5-6-fold. The other was oleomargarine as a butter substitute. While oleomargarine had been around for a long time, its generally poor quality, the availability of butter at a relatively low price, and a 10¢/lb federal tax if it was colored, kept it from becoming very popular. Consumer demand, along with the political clout of the rapidly increasing number of soybean farmers, resulted in the tax finally being repealed in 1948. The soybean's time had come; Figure 1 (3) shows how far it has progressed in the United States. We are familiar with the more recent phenomenal increase of soybean production in other countries, particularly Brazil.

The first major use of soybean oil was in margarine

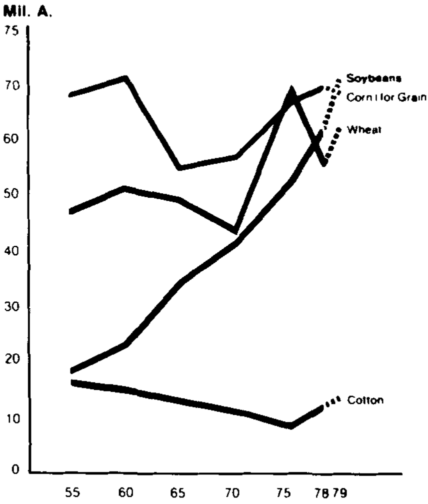

FIG. 1. Harvested acreage of U.S. crops (1955-1979).

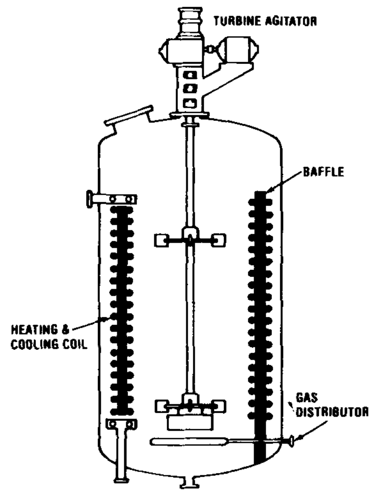

FIG. 2. Hydrogenation convertor (dead-end design).

formulation. In only about 5 years (1948-1953), soybean oil became the principal margarine ingredient. Usage in shortening also began increasing but at a somewhat slower rate, because of soybean oil's high C-18 composition which caused poor appearance and plasticity at high levels. The last big U.S. market that soybean oil conquered was as a replacement for cottonseed oil in salad oil. Attempts began in the early 1960s and attained a near 90% success in a very short time.

Increased use of soybean oil has always been paralleled by an increase in hydrogenation. This is because the degradation products of soybean oil's linolenic (triunsaturated) ester gives it an unacceptable flavor which cannot be effectively removed by deodorization, thus preventing its raw use in most fats and oils products. Fortunately, a light hydrogenation overcomes the flavor instability.

Most fats and oils are hydrogenated today in equipment that William Normann would probably recognize. A closed vessel, as shown in Figure 2 (4), is ca. 3/4 filled with the feedstock. The oil is heated to reaction temperature with steam passing through internal coils. A slurry containing nickel catalyst is pumped into the vessel and hydrogen is introduced at the bottom. Vigorous mixing with a turbine agitator keeps the hydrogen broken into tiny bubbles. Accepted theory is that a portion of the hydrogen dissolves in the oil. This dissolved hydrogen, when it combines with the catalyst, is capable of molecular addition at a double bond (unsaturation point) in the oil. Because the reaction is exothermic, the temperature of the reactants increases to a point at which the hydrogenator wishes to cap it. This usually is accomplished by cooling with water circulating through the same internal coils initially used to convey steam for heating.

The hydrogenation reactor is one unit process in a series of operations that are combined in the hardening plant. Figure 3 is a flowsheet for a typical edible oil hardening plant (5). As mentioned previously, the hydrogenation vessel (commonly called a converter) receives unhydrogenated

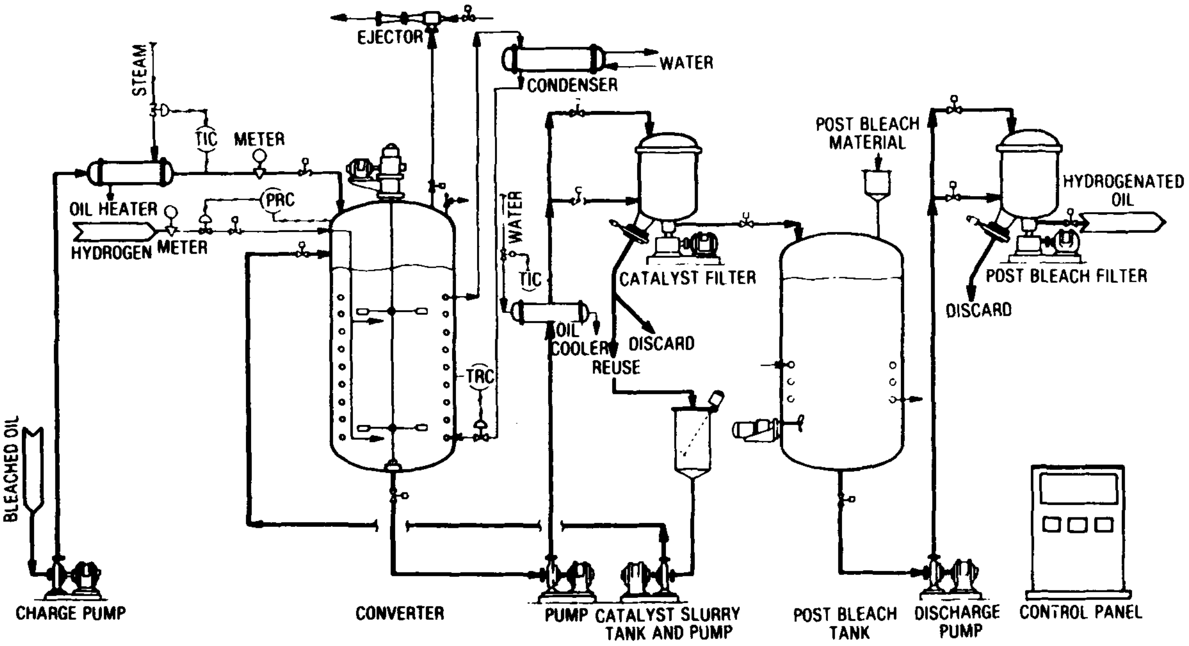

FIG. 3. Edible-oil hardening plant.

oil, hydrogen and catalyst. It is serviced by electricity (for the agitator), a vacuum system (for drying and hydrogen evacuation), steam (for heating) and water (for cooling). Prior steps (not shown) include hydrogen generation, feedstock purification and catalyst preparation. Subsequent steps, which are shown in Figure 3, include cooling and catalyst removal.

Figure 4 is part of a hardening plant flowsheet that includes a heat recovery tank (6). The thermal exchange between the incoming cold feedstock and the hot, hardened fat saves both steam and cooling water. Considering the constantly increasing cost of fuels, all hardening plants built in the future probably will include similar energy-saving features.

The reactors referred to so far have been the dead-end batch type. The first ones (ca. 1910) held one ton or less and 5-10-ton reactors were common until the 1950s. Currently, 20 and 30 tons are standard sizes. The first is a tank wagon quantity and the second, conventional tank-car size.

While dead-end batch converters presently dominate the industry, there are other quite different engineering approaches. Some are presently being used and still others may become significant in the future. Continuous hydrogenation has been practiced commercially by Procter & Gamble for a long time. The basic design of P&G's system is revealed in their 1950 U.S. Patent (7). Basically, the converter consists of a series of separate reaction zones having a very high degree of stirred agitation. The oil proceeds by a tortuous path past each agitator and baffle and then through perforated annular disks from one reaction zone to the next. The annular disks compartmentalize the reaction zones and thus serve to prevent back-mixing. Reaction rate is typically 10 iodine value (IV) units reduction/min. This translates into ca. 3-min hydrogenation time for soybean oil hardened to 105 IV. According to the patent, the very fast reaction resulting from both the exceedingly high agitation and the isothermal conditions produces fewer *trans* isomers than in conventional equipment and with only a minor preferential selectivity penalty.

A continuous hydrogenation system also is operating at the Gold Kist refinery in Marks, Mississippi. This design originated with R.R. King, who sold the rights to Dravo. Their 1974 U.S. Patent (8) process is shown in Figure 5. Note that catalyst is metered into the feedstock. The basic design of the hydrogenation reactor is a flow-through pipe with the length being adjusted depending on the amount of IV reduction desired. Measured stoichiometric amounts of hydrogen are added in increments to the oil as it moves through the system. As this plant has been operating successfully for several years, the design obviously is technically acceptable and economically satisfactory.

Lurgi also has a continuous hydrogenation system and several commercial units for fatty acid hydrogenation are in operation around the world. The Lurgi design is illustrated in Figure 6 (9). Schmidt (10) outlined Lurgi's reaction as used for partial hydrogenation. The reactor contains 16 trays with flow apertures that, in effect, serve as 16 separate reaction chambers. This is designed to prevent back-mixing, the bane of continuous hydrogenation systems. Apparently, no commercial Lurgi plants partially hydrogenate triglycerides.

Buss, a Swiss engineering firm, has a radically different approach to slurry hydrogenation, as illustrated in Figure 7 (11). Agitation is achieved by entrainment of hydrogen into a liquid/catalyst slurry circulated through a Venturi nozzle at high velocity. The nozzle acts as an eductor, and the action of the slurry passing through creates gas/liquid/solid mixing to a degree which far exceeds conventional turbine stirring. Activity should be excellent, but there are un-

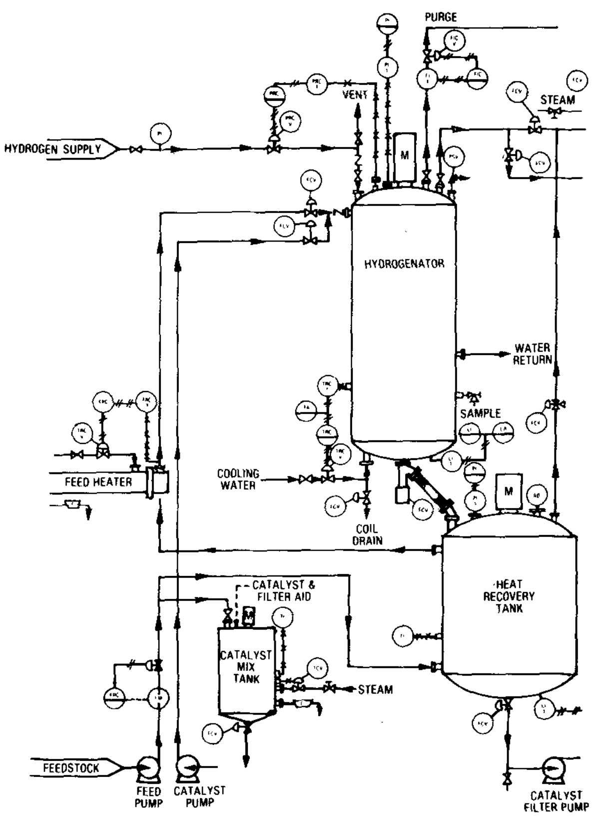

FIG. 4. Hydrogenation with heat recovery.

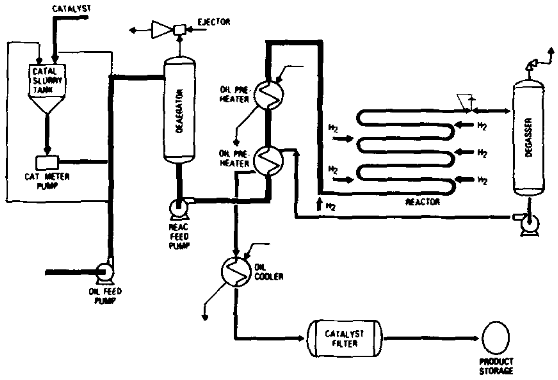

FIG. 5. King/Dravo process.

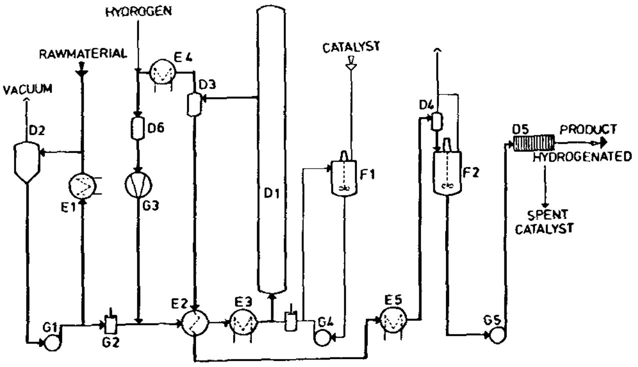

FIG. 6. Continuous hydrogenation of fatty acids.

answered questions about both preferential and *trans* isomer selectivity. While commercial plants are operating in Europe and South America, very little has been published about the characteristics of the hydrogenated oil.

Fixed-bed hydrogenation of triglycerides has received very little attention up to this time. This may seem surprising, considering that fixed-bed processes are the norm in the petrochemical industry. The principal reason it has always been considered impractical is the belief that the impurities in vegetable oils would quickly coat ("gunk up") the exterior of fixed-bed catalyst particles, thus rendering the catalyst inactive for all practical purposes. Assuming this objection could be overcome, and I believe it could if the approach offered sufficiently enticing economic or nutritional advantages, what would be the characteristics of the hydrogenation reaction? Theory indicates, and limited bench scale work confirms, that the reaction would be exceedingly fast because of the very high catalyst concentration at the point of contact. From experience with slurry systems, we know that a faster reaction means less preferential selectivity as well as less *trans* isomer formation. In a fixed bed, the reaction is so fast that there is almost no ~~prefer~~ential selectivity nor *trans* isomer formation.

Depending on the eventual outcome of the current *trans* isomer and saturated fat controversies, fixed bed hydrogenation could be a technique making it possible to manufacture margarine and shortening having the physiological and nutritional properties determined to be the most healthful.

What are the advantages and disadvantages of continuous hydrogenation, whether slurry or fixed bed? First, the advantages are (a) saves money by being more energy-independent; (b) more uniform selectivity because of a more isothermal reaction; and (c) eliminates equipment problems inherent in batch cycling. Disadvantages are (a) contamination when changing products; (b) more dependent on instrumentation reliability; (c) WNDITWB (we've never done it that way before).

What is the probability of any of these unconventional hydrogenation systems making a major impression in the fats and oils industry in the 1980s? Except for Procter & Gamble, who already have their system, but give no indication of marketing the design, I do not predict that any of the other fats and oils processors will devote the time and money required to design and build their own. The processor's philosophy is to buy turn-key proven equipment, as they already do with filters, deodorizers and centrifuges. This leaves it up to the engineering/equipment companies. As already discussed, several of them (Dravo, Lurgi and Buss) already have tried "new" converter designs. While each company has a slightly different set of problems, the decisions and appraisals they must make consider expense, personnel and profit.

Expense involves building and maintaining a pilot, or demonstration plant, combined with suitable analytical facilities than can demonstrate the economic performance of the system, and the characteristics of hydrogenated products.

Personnel includes those assigned on an uninterrupted basis to resolve the mechanical, technical and economic problems that are inevitable in commercializing any new engineering concept.

Profit probability must be sufficient to convince an engineering or equipment company that there will be an opportunity to sell enough units at a profit sufficient to pay off the development costs within a reasonable time. It is the same economic hurdle with which we are familiar as it applies to new models of airliners. Boeing made it by selling enough 747s. The English and French missed with the Concorde.

The practical definition of a salad oil is that it remains liquid in a refrigerator. The official definition is that it passes the cold test (AOCS Method Cc 11-53). However, there is a catch. As referred to earlier, the degradation products of soybean oil's linolenic (triunsaturated) ester give it any unacceptable flavor which cannot be effectively removed by deodorization. Also mentioned was that this shortcoming can be overcome by a light hydrogenation. Specifically, this means lowering the linolenic content from nearly 9% to ca. 3%. This is accomplished by reducing the IV to under 110. This "brush" hydrogenated oil must then be winterized to regain its salad oil characteristics. The name of the economic game is to obtain as high a salad oil yield as possible after winterization. Conditions and procedures of the hydrogenation are important in this regard. Conditions

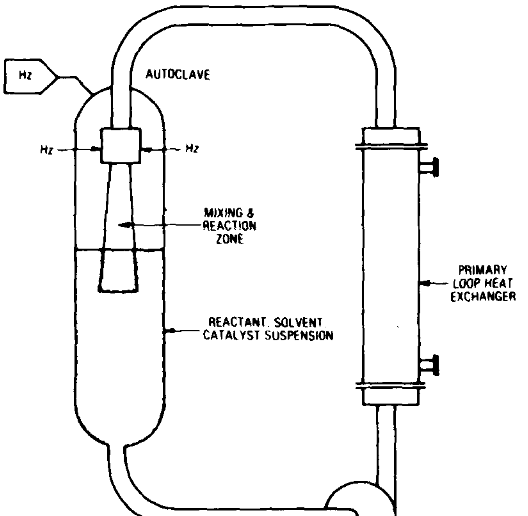

FIG. 7. Loop hydrogenation reactor.

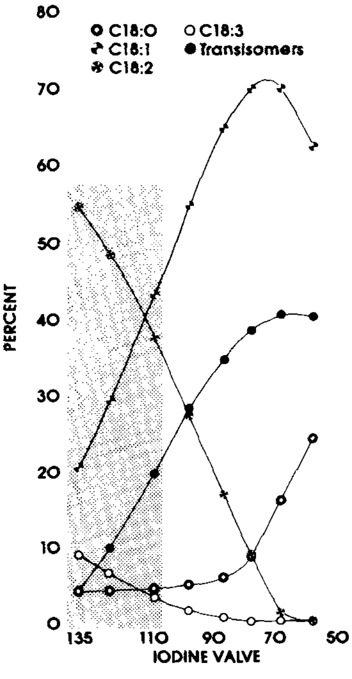

FIG. 8. Hydrogenation of soybean oil at 140 C and 3 atm $H_2$ pressure with 0.02% catalyst as Ni.

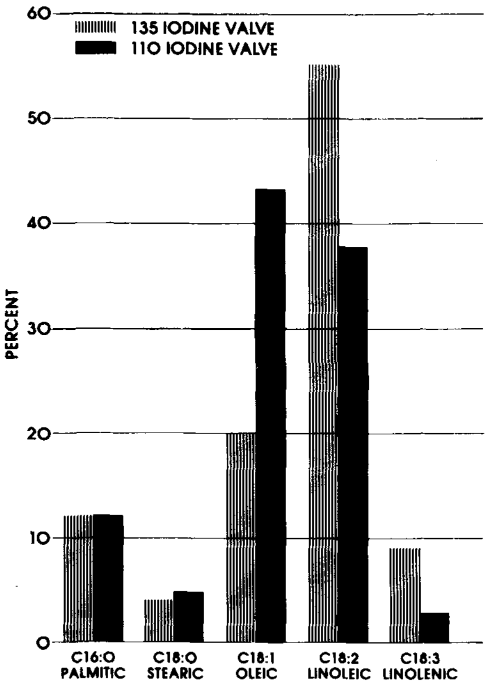

FIG. 9. "Brush" hydrogenated soybean oil.

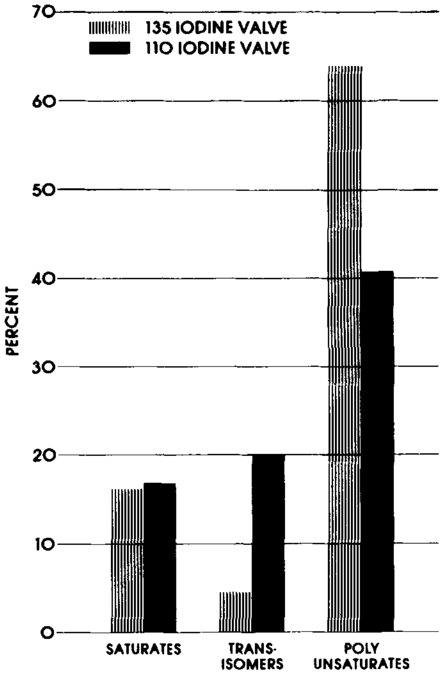

FIG. 10. "Brush" hydrogenated soybean oil.

should be chosen that make the least possible saturates and form the least possible *trans* isomers. The hydrogenator can influence these factors by the choice of catalyst and by the hardening conditions used. Commercial nickel catalysts vary considerably in their inherent preferential selectivity. Only the most selective should be chosen for this application. Also, only fresh catalysts should be employed because used catalyst is always less preferentially selective and makes more of the elaidic (*trans*) isomer.

Unfortunately for hardening conditions, those which give the best preferential selectivity (low pressure and high temperature) also promote *trans* isomer formation. The good news is that, under most hardening conditions and when using a fresh catalyst that is inherently quite selective, few saturates are formed above 100 IV. Therefore, hardening conditions usually are chosen which help suppress *trans* isomer formation. In other words, hydrogenation is done at low temperature (140-160 C) and the highest pressure avail-

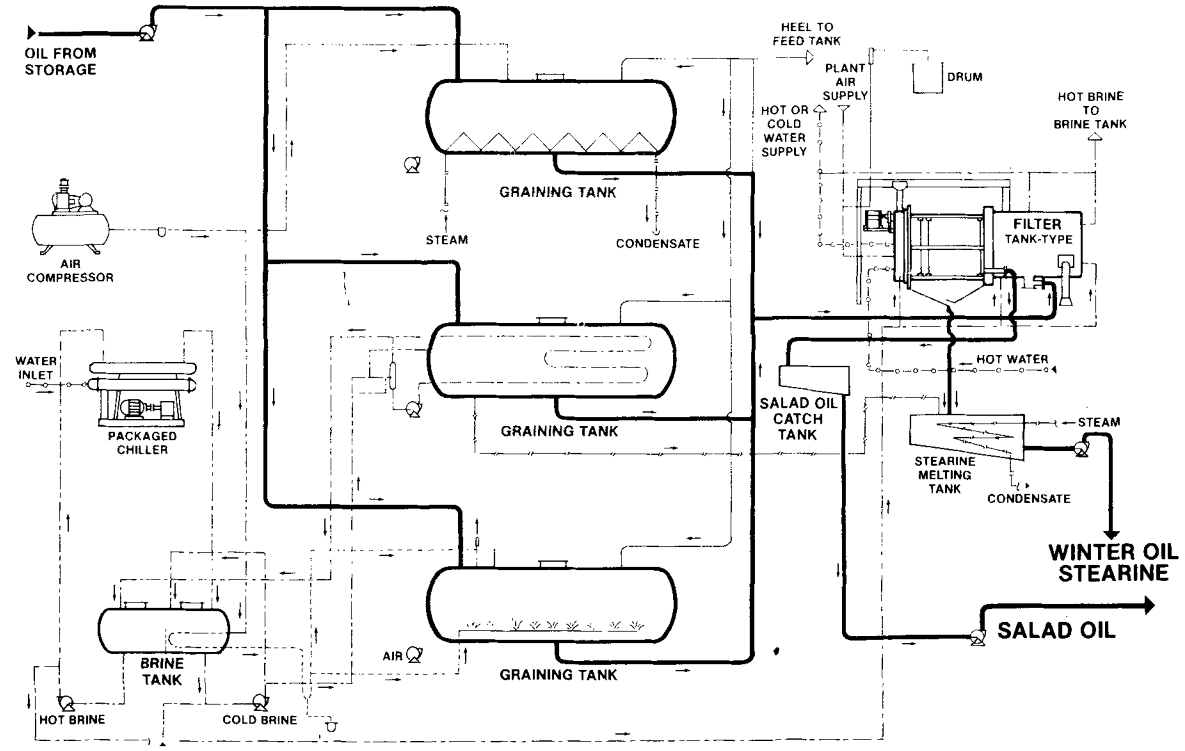

FIG. 11. Winterizing flowsheet.

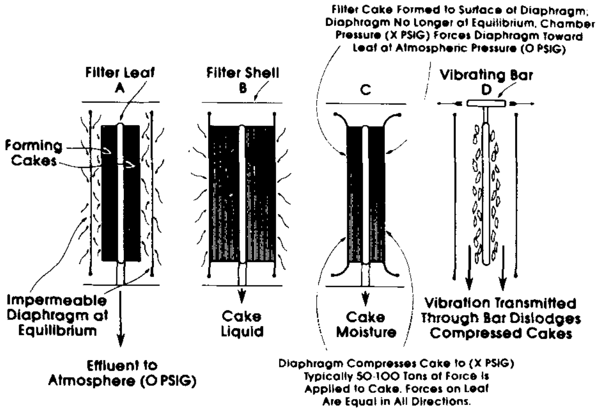

FIG. 12. Diaphragm filter.

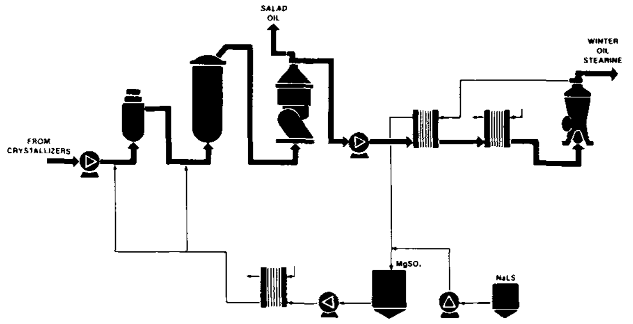

FIG. 13. Centrifugal separation.

able that the equipment will stand. Three to 5 atmospheres is common. Figure 8 (12) depicts ester composition and *trans* isomer results when hydrogenating soybean oil at these type conditions. The shaded portion is the IV range of interest.

Figure 9 shows values from Figure 8 comparing the original and 110 IV oils. We observe that, while the linolenic was being reduced from 9% to an acceptable 3%, stearic increased only from 4 to 4.5%. This very slight increase in stearic should subsequently cause only a correspondingly small amount of crystalization during winterization.

In Figure 10, we see the considerable increase in *trans* isomers (from 4% to 20%) between 135 and 110 IV. This elaidic ester, which melts at 43.7 C, is the principal source of winter oil stearine formed during winterization.

Winterization of lightly hydrogenated soybean oil is not essentially different from the winterization of cottonseed or other oils requiring chilling and separation to become salad oils. Figure 11 is a flowsheet of a typical winter oil plant (13). The graining tanks require means to heat, chill and agitate the oil. Briefly, the oil is cooled at ca. 0.5 C/hr to ca. 7 C where it is held 8-12 hr for crystallization to be completed. It continually undergoes very slight agitation. Crystal inhibitors usually are added to increase crystal size and thus facilitate filtration.

Techniques and equipment for separating the winter oil (salad oil) from the winter oil stearine vary considerably. Figure 11 shows a conventional tank type filter. There are still some plants using plate and frame filter presses. Vacuum filters are highly regarded (14). One filter company has recently begun to market a diaphragm-type tank filter. Figure 12 illustrates its operation (15).

Centrifugal separation of the oil and stearine also is commercially practiced. It is a basket technique that spins off the oil while the stearine remains in the basket. When the stearine accumulates to a certain point, centrifuging is stopped and the stearine is mechanically scraped from the basket. It is a cycling operation.

Recently, a continuous centrifugal approach has been introduced. A process flowsheet is shown in Figure 13 (16). Briefly, an aqueous solution made up of a wetting agent (sodium lauryl sulfate) and an electrolyte (magnesium sulfate) is mixed into the stream coming from the crystallizers (graining tanks). The salad oil is separated in a centrifuge. The heavy aqueous stearine fraction is then heated, which melts the stearine and allows it to be separated in a second centrifuging step. The aqueous solution containing wetting agent and the electrolyte can then be recycled after cooling. An interesting aspect of this technique is that while it was developed for separating palm oil into fractions, it may be equally applicable for salad oil.

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