a) corrosion effects on equipment, b) by-products waste, and c) high acidity of refined oil.

The acid refining is concerned mainly with the use of sulfuric acid in concentrations of 50-85%. The equipment should be lead-lined tanks for batch operation, with steel or wood to support the lining. Agitation may be mechanical or through the use of air sparge.

The oil is treated with quantities of acid ranging from .1 to 2% depending upon its crude condition. Temperatures of 80-120°F. are used; cooling is applied whenever exothermic conditions become evident. The diluted acid does not sulfate the oil but has a severe charring action on the other organic material present. This action manifests itself in the formation of black particles which coalesce and precipitate to form a tarry residue. After sufficient settling time, the oil is siphoned off and sometimes given a lime treatment to neutralize residual acid. More frequently it is thoroughly washed and dried in the usual manner. Bleaching is also accomplished as previously described. The acid residue is discarded as no commercial use for it has been developed as yet.

Refining Equipment

Batch Method. The equipment for this method may be either open or closed-top tanks fitted with conical bottoms. Two-speed agitation of 20-40 r.p.m. is used with enough mixing blades on a vertical shaft to insure thorough contact of oil and treating agents as well as wash water. Spray rings are located at the top of the tank for addition of refining agents and water. Coils or jackets may be used for steam or water heating and cooling.

Continuous Method. The oil and refining solution are metered continuously for proper proportioning. The two liquids are then introduced to a mixing chamber, where vigorous agitation insures complete and thorough contact for soap formation. The mixture then passes to a heating chamber to prepare the soap for proper processing. The combination next flows to the soapstock centrifuges where continuous separation of oil and soap occurs. The soapstock is discharged to a catch tank while the oil flows to the water mixing chamber. Here it is washed by rapid mixing with hot water and properly metered, prior to passing to the water-wash centrifuges where separation of oil and water takes place. Single or double water-washing stages may be employed depending upon the requirements of the refiner. The oil next flows to the vacuum flash drier, where the residual moisture (approx. .15%) is removed continuously and the oil is pumped to bleaching tanks.

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Fractionation of Drying Oils and Acids

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DURING the past 10 to 15 years good chemical engineering has been combined with drying oil technology to produce a number of methods of increasing the degree of unsaturation of a fatty oil or fatty acid. An attempt will be made to briefly review those methods of fractionation which are currently in commercial operation. It is obvious that only the general principles of operation can be covered in this one 40-minute session.


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These processes may be divided into the following classifications:

- a) liquid-liquid fractionation
  - 1. furfural process
  - 2. liquid propane process
- b) fractional crystallization
- c) fractional distillation

The products produced by these processes have aided the drying oil chemist in his choice of raw materials.

Liquid-Liquid Fractionation

Furfural Process. Liquid-liquid fractionation of a glyceride oil with furfural is dependent upon the fact that oils are only partially miscible with furfural at normal temperatures. If the temperature were to be raised, complete miscibility of the oil and furfural would eventually result and the process would become inoperable. When a glyceride oil and furfural are contacted however, at a temperature below that of complete miscibility, two phases are obtained, a solvent predominant phase and an oil predominant one. It has been found (1, 2) that the more unsaturated glycerides concentrate in the solvent predominant phase, or so-called extract phase, with the more saturated glycerides in the oil predominant or raffinate phase. The degree of separation effected by a single stage batch separation is rarely sufficient in producing fractionations of commercial significance. Separations of this type require multiple batch separations or continuous countercurrent extraction with the use of reflux.

In order to obtain efficient fractionation it has been found that continuous countercurrent methods are the most economic. A simple countercurrent system is illustrated in Figure 1 (3).

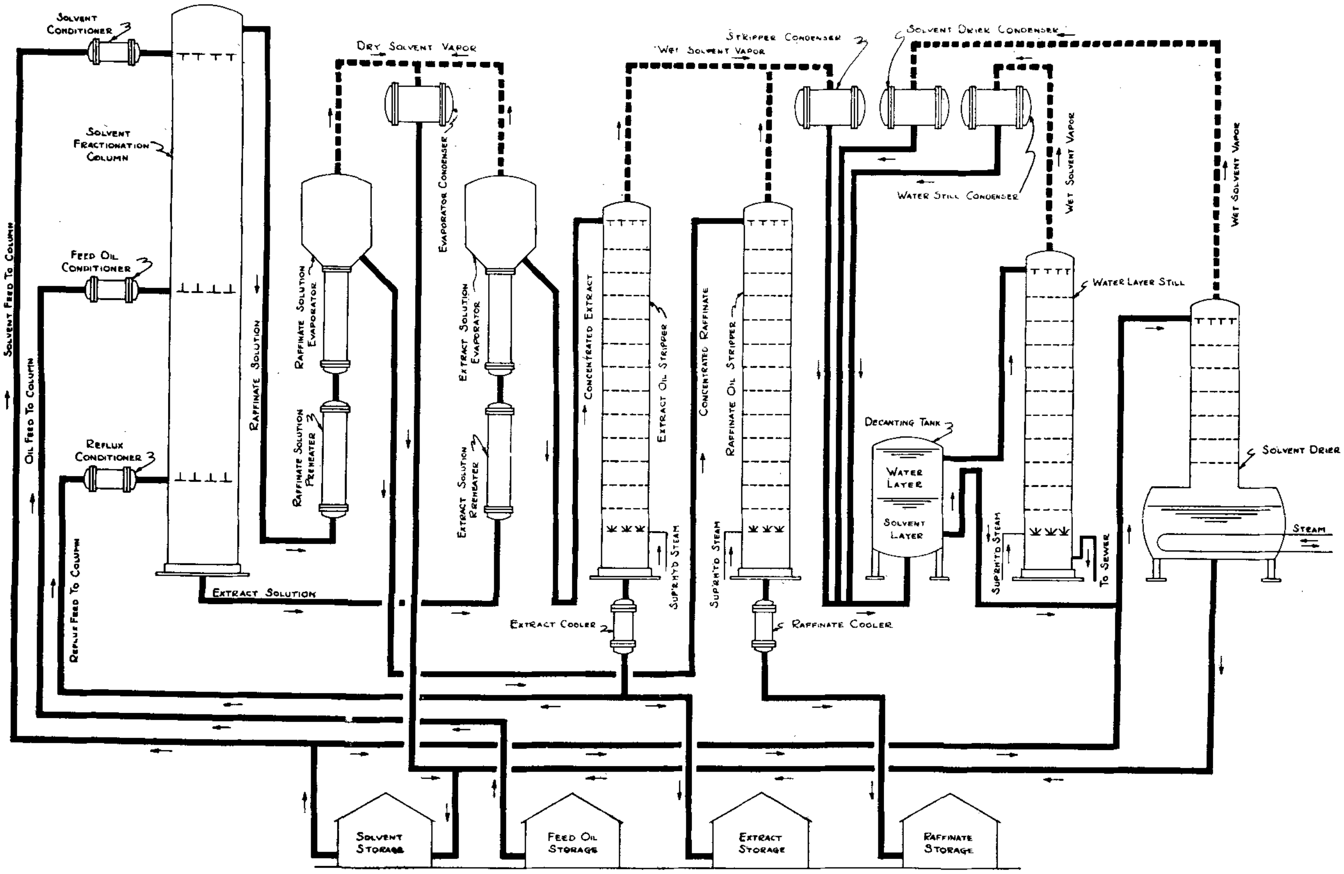

FIG. 2. Furfural process—Flow sheet.

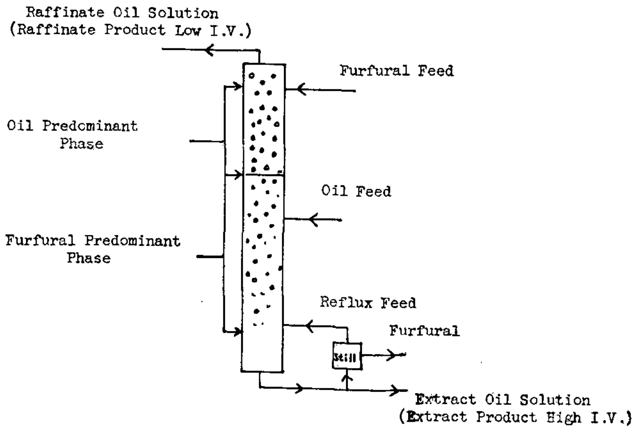

FIG. 1. Furfural fractionation column.

The column is packed with Raschig rings or Berl saddles, so that a free space or settling chamber is allowed at both ends of the column. Furfural is introduced near the top, usually in a ratio of 3 to 14 parts per part of feed oil, and travels downward countercurrent to the rising oil. Oil is introduced at an intermediate point between the furfural and reflux feeds.

Part of the extract product oil is fed into the bottom of the column as reflux. This is important to obtain a high iodine value product and cannot be achieved as efficiently in any other way. Naphtha may be used in place of extract product oil as a reflux medium; however less efficient results have been obtained with the use of naphtha.

An interface is generally maintained between the oil feed and the solvent feed, with the oil phase predominant in the upper part of the column and the furfural phase predominant in the lower part. The furfural then falls in droplets through the upper, oil-predominant phase, and the oil conversely rises in droplets through the furfural-predominant phase. The interface is controlled by using an overflow leg on the column or by throttling the flow of extract solution from the column.

Figure 2 shows in simplified form the flow sheet of a plant at present handling a tank car of feed oil a day. It is obvious by comparison with the previous figure that the process is largely one of solvent recovery.

The raffinate of low iodine value (I.V.) fraction flows out of the top of the column to a flash evaporator operating at 100 mm. mercury vacuum where the greatest amount of solvent is removed. The concentrated oil-furfural solution then passes to the top of a bubble-plate stripping column which is operated under 50 mm. mercury vacuum and into which superheated steam is passed at the bottom. In this unit the solvent is completely removed from the oil.

The extract solution passes out of the column at the bottom and likewise is fed to an evaporator and stripper. Part of the stripped extract oil is returned to the column as reflux, the remainder sent to extract storage.

The furfural from the evaporator condenser is free of water and is sent directly to solvent storage; however that from the stripper condenser also contains water from the condensed stripping steam, and this mixture is sent to a decanter tank where the water and furfural are separated into immiscible layers. Water and furfural form a minimum boiling mixture which makes a convenient system for obtaining anhydrous furfural. The water layer containing approximately 8% furfural is pumped to the top of a bubble-plate still operating at atmospheric pressure, and superheated steam is passed into the bottom. The azeotropic mixture is distilled and caught in the decanter where it again layers out into a water and a furfural layer. The excess water from the still passes to the sewer.

The wet furfural layer from the decanter containing approximately 5% water is sent to a vacuum dryer operating at 100 mm. mercury pressure, in which the azeotrope distills, allowing the dry furfural to return to storage.

Until recently it had been impossible to obtain the degree of fractionation in larger columns that had been obtained in two-inch and three-inch diameter pilot plant columns. Within the last few months it has been determined that by proper arrangement of the packing within the larger columns more efficient fractionations could be obtained, which were essentially equivalent to those produced in smaller columns. These fractions are shown in Table I.

TABLE I

Column Used	Solvent: Feed Oil Ratio	I.V. Extract	I.V. Raffinate
3″ diameter	8.3 to 1	150.7	102.7
22″ diameter	8.3 to 1	150.1	104.0

In all runs at the present time a single column system is employed and degummed soya oil is used as a feed stock. Furfural not only acts as a preferential solvent for the unsaturated glycerides but also for free fatty acids, chlorophyll, other natural pigments, and unsaponifiable matter. These coloring pigments remain in the extract in a one-column system and must be removed from the final drying oil by bleaching. This fraction has found use as a linseed oil replacement in both exterior and interior paint vehicles.

The raffinate or low iodine value fraction has had removed from it the major portion of the free fatty acids as well as chlorophyll and other pigments. Most of the "break" present in the original oil is concentrated in the raffinate fraction. Special refining techniques other than alkali refining have been applied to this fraction so that a fully refined oil is produced. This fraction has found use as a food oil.

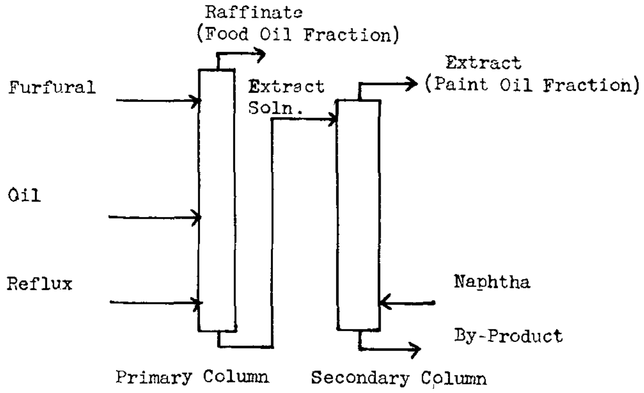

FIG. 3. Dual solvent refining process.

A dual solvent process has also been developed in order to produce a paint oil fraction which is light in color and relatively lower in free fatty acid, and a by-product fraction which is relatively rich in unsaponifiable matter (4). Fractionation of this type is conducted as illustrated in Figure 3.

In this fractionation the extract solution produced in the primary extraction column is fed to the top of a second fractionating tower. Naphtha is introduced to the bottom of this tower and flows countercurrent to the extract solution. The rising naphtha removes glyceride oil from the furfural, leaving in the polar solvent a concentrate of the free acids, coloring pigments, and unsaponifiable constituents. After the removal of solvent this by-product becomes a good source of tocopherol and sterols.

Liquid Propane Process. Propane is an odorless gas at room temperature and atmospheric pressure. Some of the significant properties of propane (5) are:

a) boiling point @ 1 atmosphere pressure, —44°F.
b) critical pressure, 643 lb. absolute @ 212.2°F.
c) specific gravity, 0.50 @ 70°F., 0.25 @ 212°F.

When glyceride oils and liquid propane under pressure are contacted at room temperature, they are completely miscible. Fractionation by means of liquid propane is accomplished by the unique fact that as the temperature approaches the critical temperature the system becomes immiscible.

As a means of illustrating this principle it has been found that tallow and propane under pressure at room temperature are completely miscible. The temperature can then be increased to 150°F., at which temperature an additional phase appears. As the temperature is increased and approaches the critical temperature of the solvent, the amount of the second phase increases. Therefore, contrary to most conceptions of increased solubility with an increase in temperature, this system shows a decrease in solubility with an increase in temperature when operating near the critical temperature.

The propane process is selective since the more unsaturated glycerides and the coloring pigments are the least soluble in the propane. In many respects this process may be thought as the direct opposite of the furfural process.

A number of liquid propane plants have been built for the decolorization of tallow and other low grade fats; however this year a plant has been put into operation for the fractionation of fish oil and is producing a fish oil fraction of increased unsaturation.

In order to describe the operation of a plant of this type it may be well to start with the simple decolorization of tallow even though it is not a drying oil. A simplified flow diagram (6) is shown in Figure 4.

The crude oil is pumped to the middle of the column and liquid propane enters at the bottom. The propane is pumped to the tower at sufficient pressure to keep it in liquid form at the desired operating temperature. The temperatures in the extraction tower are regulated so that approximately 98% of the tallow dissolves and 2% flows out the bottom as an insoluble phase. In order to accomplish a separation

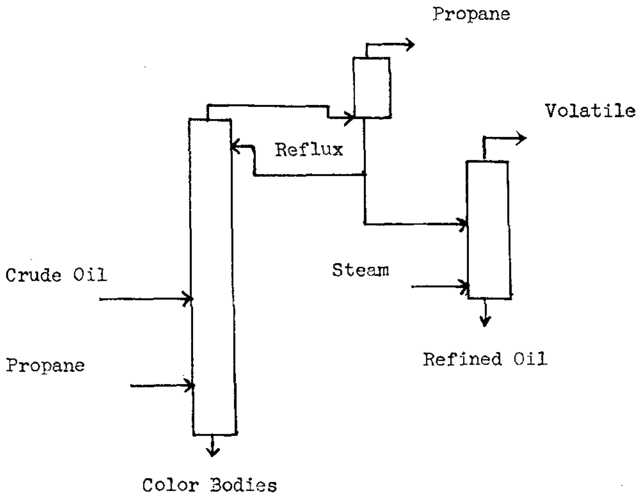

FIG. 4. Decolorization of tallow.

of this type in a commercial unit, typical conditions of operation (5) are:

a) solvent to oil ratio, 17 to 1
b) temperature, top of col. 162°F., bottom of col. 158°F.
c) pressure, 465 psig
d) reflux, none

Although the vapor pressure of propane at 162°F. is 380 psig, in operation it is recommended that at least an additional 30 pounds be added to avoid gasification in the tower. The 465 psig used commercially therefore is arbitrary, but it has been found desirable to maintain the pressure constant and vary the temperature to adjust the yields. At 120°F. it is reported that the oil and propane are completely miscible whereas at 180°F. the oil is almost completely insoluble.

Employing these principles, fish oils may be fractionated (6) into: a) vitamin concentrate, b) intermediate iodine value fraction, c) high iodine value fraction, and d) color bodies.

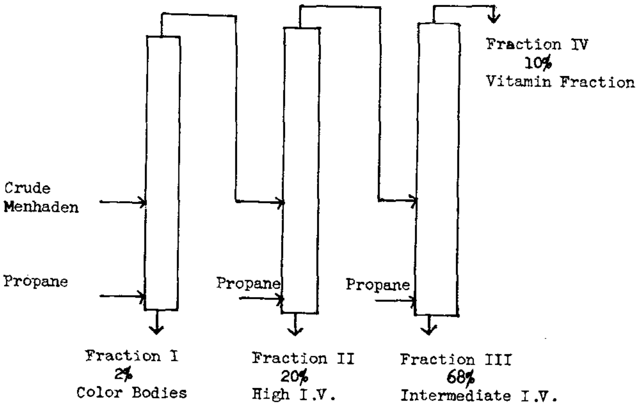

FIG. 5. Fractionation of menhaden oil.

TABLE II

Fraction	Crude Oil	Fr. 1	Fr. 2	Fr. 3	Fr. 4
% yield	......	2%	20%	68%	10%
I. V.	175	260	225	165	90
Vitamin A potency—Units	100	......	......	......	800
Color (Gardner)	11+	Black	10	4—	7

Reported fractionation of menhaden oil is shown in Figure 5.

The constants of the fractions are shown, Table II.

It has recently been reported (7) that commercial fractionation of fish oil by the propane process is in operation essentially by the system shown in Fig. 6.

Fractional Crystallization from Solvents. The separation of solid fatty acids from liquid acids has been traditionally one of mechanical pressing. This had been essentially the only process of removing solid acids from liquid acids of the same carbon chain length until the application of the process of crystallization from solvents.

In order to understand these methods of processing it probably would be best to describe the fractionation of tallow into commercial stearic and oleic acids since most of the literature (8, 9) concerns these products. Drying oil acids from soya, linseed, or fish oil may be processed in a similar manner by the solvent crystallization process.

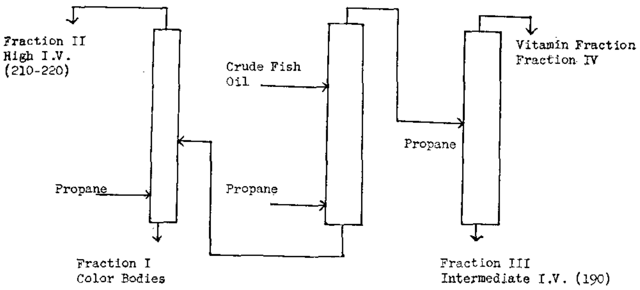

FIG. 6. Fractionation of fish oil.

Mechanical Pressing. In the mechanical pressing process the tallow is split into fatty acids and distilled and the hot fatty acids are transferred into a series of flat aluminum pans and then cooled to 36°F. The cakes of solidified fatty acids are removed from the pans, wrapped in burlap cloths, and placed in hydraulic presses. Pressure is applied, and this cold pressing operation removes the greater portion of the liquid acids. The liquid acids are known as Red oil, and the quantity of solid acids present in it depends upon the temperature maintained in the pressing operation. The solid acids are known as cold pressed cake. In order to raise the melting point and reduce the liquid acids in the cold pressed cake, it is melted and again allowed to solidify in aluminum pans. These cakes are then placed in horizontal presses where they are subjected to a slight amount of heat and pressure yielding single press stearic acid. Further hot pressing removes more liquid acids and produces commercial double pressed stearic acid. This product is approximately 45% stearic and 55% palmitic acid.

The liquid acids removed in the hot pressing contain considerable quantity of solid acids and are recycled with the original fatty acids.

Solvent Crystallization. The mechanical pressing method is both expensive and a messy operation. For this reason efforts had been made to reduce the cost of operation, increase the efficiency, and eliminate the messy operation. Laboratory results indicated that this could be accomplished by means of crystallizing the solid acids from a solvent solution.

The commercial success of a solvent crystallization process was dependent on developing a continuous process. The process required that the following operations be done on a continuous basis: a) preparation of feed, b) crystallization, c) refrigeration, d) filtration, and e) solvent recovery.

It had been determined that one of the most desirable solvents for use in this work was 90% methanol since it formed easily filterable crystals at not too low temperatures. A simplified flow sheet of this process is shown in Figure 7.

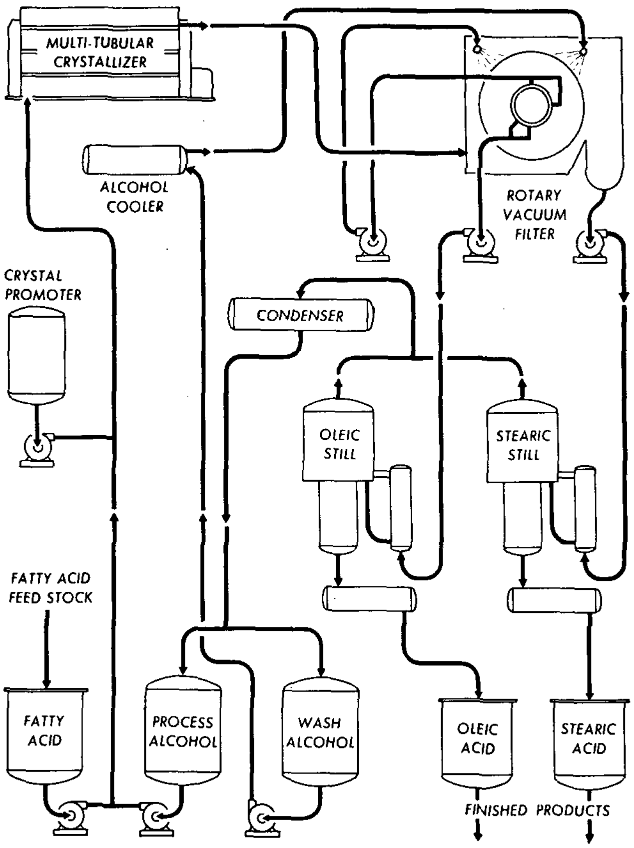

FIG. 7. Emersol process—Simplified flow sheet.

Distilled fatty acids are generally employed as a feed stock. These acids together with the solvent and a small amount of neutral fat which is added as a crystal promoter are pumped to a specially designed continuous crystallizer. The crystallizer is a multitubular unit equipped with internal scrapers for promoting heat transfer. These tubes are jacketed, and cold antifreeze solution of similar composition to the crystallizing solvent is pumped countercurrently through the jackets.

The slurry mixture after leaving the crystallizer flows to a totally enclosed rotary vacuum filter which is installed in a refrigerated and insulated cold room. During filtration the solid fatty acids are continuously washed with fresh solvent to remove mother liquor containing liquid acids. A hot solvent wash maintains the filter cloth in proper condition for continued maximum production.

The filter cake is transferred to a melter, from which it is pumped to a still for solvent recovery. The solvent is likewise continuously removed from the filtrate containing the liquid acids.

Fractionations (9, 10) reported on drying oil acids are given in Table III.

In general the original fatty acids employed are prepared from soap stock obtained in the alkali refining of vegetable oils or from other low grade sources.

Fractional Distillation. Fractional distillation may not be applied to glycerides as such because of their high boiling point; however this technique may be employed with the component fatty acids or monoesters of these fatty acids.

TABLE III

Fatty Acids	I.V. Original	% Solid Acids	I.V. Solid Acids	% Liquid Acids	I.V. Liquid Acids
Linseed	185.0	14	87	86	195.0
Soya	129.0	14	7-12	85	155-158
Sardine	160.0	25	30	75	201.5
Cottonseed	103.0	30	7-12	70	142-144

In the preceding discussions of fractionation by liquid-liquid or fractional crystallization techniques the segregation was effected on the basis of differential solubilities as caused by varying degrees of unsaturation. In distillation the fractionation produced is almost entirely according to molecular weight or chain length. Fatty acids of a given chain length show very slight differences in volatility with differences in unsaturation and therefore make a separation of compounds such as oleic and stearic acid virtually impossible by distillation. There is however quite marked differences in volatility between two fatty acids of different chain length.

While fractionation of a fatty acid mixture cannot be made on the basis of unsaturation alone, it still is possible to produce fractions of higher iodine value than the parent compound. This is possible because the saturated fatty acids of cottonseed oil, soya oil, and other vegetable oils are preponderantly palmitic acid, a C_{16} fatty acid. Therefore by removing as a first cut the C_{16} saturated fraction of mixed cottonseed acids, the remaining cuts will be higher in iodine value because of the reduction in saturated acids.

The fatty acid composition (11) of a number of oils is given in Table IV.

TABLE IV

Per Cent	Coconut	Cottonseed	Soya
Caprolic (C^6)	0.5	......	......
Caprylic (C_8)	9.0	......	......
Capric (C_{10})	6.8	......	......
Lauric (C_{12})	46.4	......	......
Myristic (C_{14})	18.0	1.4	0.3*
Palmitic (C_{16})	9.0	23.4	9.8
Stearic (C_{18})	1.0	1.1	2.4
Arachidic (C_{20})	......	1.3	0.9
Tetradecanoic (C_{24})	......	0.1	0.1
Hexadecanoic (C_{26})	......	2.0	0.4
Oleic (C_{18}; 1 $C{=}C$)	7.6	22.9	28.9
Linoleic (C_{18}; 2 $C{=}C$)	1.6	47.8	50.7
Linolenic (C_{18}; 3 $C{=}C$)	......	......	6.5

* Myristic or lower.

From Table IV it can be seen that coconut fatty acids can be separated with comparative ease because of the diverse composition of this oil. The high palmitic ratio in cottonseed oil acids likewise makes it more readily separable by distillation than soya oil.

One method of fractional distillation of cottonseed acids (12, 13) is that described in Figure 8.

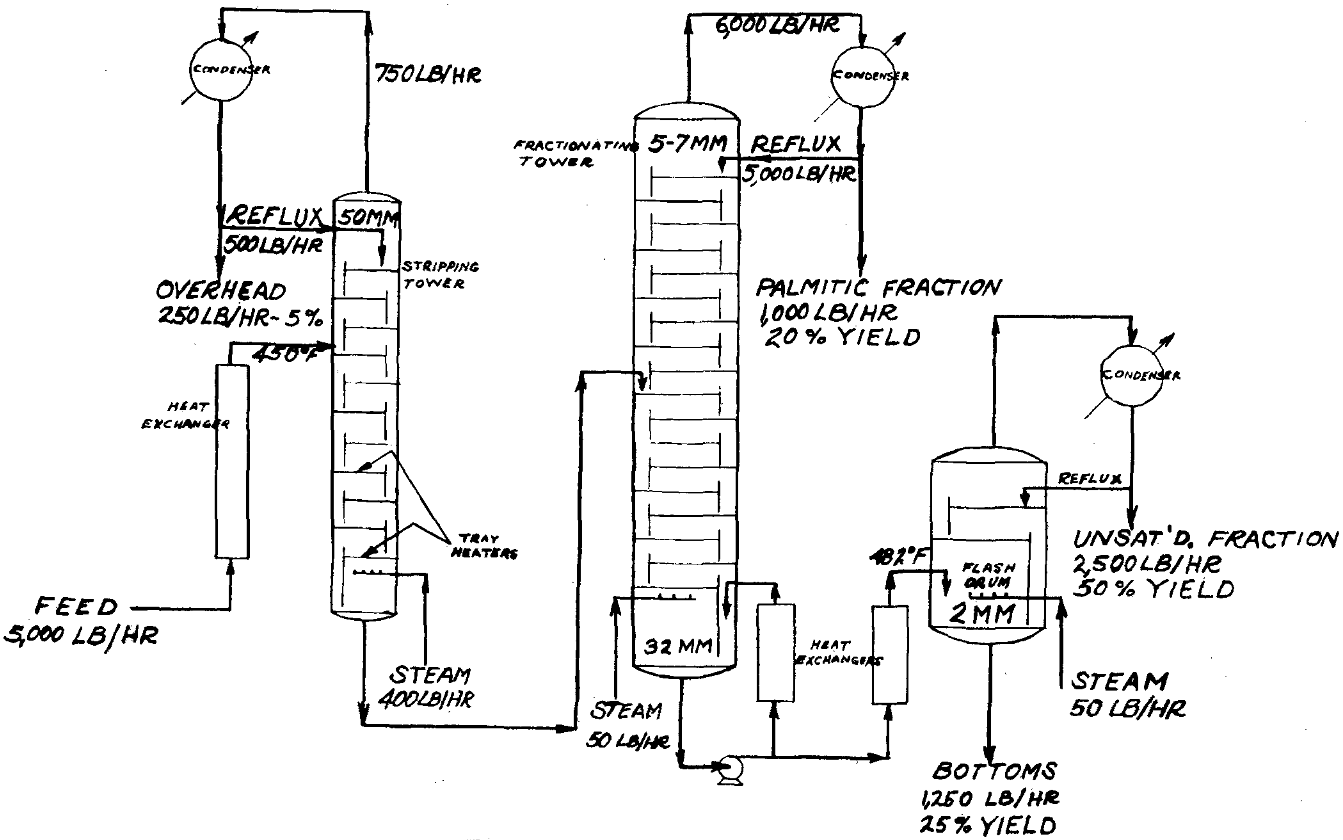

FIG. 8. Distillation of cottonseed foots.

Acidulated cottonseed foots containing 90% or higher free acids is pumped through a heat exchanger and enters the stripping column at approximately 450°F. This column is maintained at approximately 50 mm. Hg. pressure. The stock passing down over a series of trays is met by a countercurrent of stripping steam amounting to approximately 400 pounds per hour. The vapors pass off the stripping tower at a rate of approximately 750 pounds per hour and are condensed, 250 pounds per hour being removed as product and 500 pounds per hour being returned to the top of the stripping column as reflux.

The main portion of the original feed, which has been stripped of non-condensable gases, air, moisture, and low boiling impurities, is fed to the fractionating tower. The pressure in this tower is maintained at approximately 6 mm. Hg. at the top and 32 mm. Hg. at the bottom. Part of the bottoms from the fractionating column are recycled through a heat exchanger and returned to the lower portion of the tower.

The remaining bottoms from the fractionating tower comprise the unsaturated fraction, and these are drawn into a flash drum maintained at approximately 2 mm. Hg. pressure. The process is so operated that approximately 2,500 pounds per hour of distillate are obtained.

The bottoms from the flash drum are removed as soft pitch and stored for subsequent rerunning for the removal of any volatile fatty acids and to harden the pitch.

The quantity of palmitic acid removed from the top of the fractionating tower is approximately 6,000 pounds per hour, of which 1,000 pounds per hour is removed as product and 5,000 pounds per hour is returned to the top of the tower as reflux.

By means of fractional distillation the following types of more unsaturated acids are obtained:

TABLE V

Original Stock	I.V. Original	I.V. Concentrate
Cottonseed foots	100	135-140
Soya foots	130	147
Sardine oil	190	235

The above fatty acids (Table V) have found use in alkyd resin preparations. The cottonseed acids, due to their low linolenic acid content, have found use in the preparation of non-yellowing finishes. Fractionated soya acids have found use in finishes where improved drying rates over whole soya oil acids are necessary or desirable.

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