matrix of small crystals of lower melting point, which holds the liquids. The chilled portion enters this pre-crystallizer at a temperature of about 50 to 55°F. while the warm stream is about 100°F. The mixture enters the ''A'' unit then at about 85°F. The chilled material which is not recycled passes through screens or plates to give the product some amount of work and then is allowed to set in the quiescent ''B'' unit before going to the printing and packaging machine.

A Turgasen patent (6) describes a process which does not use the closed continuous internal chiller. It resembles the churning procedure used for making butter. Melted fat and milk in a ratio of about 1 part fat to about 2 parts milk are pumped into a tank; steam is injected into the line in the direction of flow. This steam injection raises the temperature to about 250°F. and disperses the oil phase into a fat-in-milk emulsion. This mixture is introduced into a vacuum vessel where the emulsification action is completed and a heavy creamy emulsion results. This emulsion is cooled, employing a regular milk cooler, to a temperature below the melting point of the fat. This emulsion is then churned in conventional butter churns at a temperature favorable to the aggregation of the fat globules. When the aggregates reach the proper size, the emulsion breaks and the fat separates into a plastic mix containing about 14% water. The excess milk is drained off, and the fat portion may be washed with cold water. The moisture content is adjusted, salt is added, and this plastic product is churned until the desired texture is obtained. The product is then removed from the churn, placed in trucks, and tempered for several hours before printing and packaging.

The Packaging of Edible Fat Products. In the case of lard and shortening, fillers are positive displacement volumetric machines. They are made in a high-pressure type and a low-pressure type. The high-pressure type fillers employ a pump which fills a calibrated cylinder and, with the proper valving, forces the product out of the cylinder by the incoming product on the opposite side of the piston. At the completion of the stroke the action is reversed. The product is delivered through an extrusion valve to the package. The low-pressure type filler also employs volumetric displacement, but it does not rely on a product pump to operate the measuring cylinders. This type of filler employs a rotating table onto which the empty tin is fed. A feed hopper rotates above it. The plastic feed is delivered to this hopper at about 300 to 400 p.s.i.g. and is discharged into this hopper at substantially atmospheric pressure through an extrusion valve. The hopper is equipped with stationary plow-type arms to prevent the fat from setting up. The measuring cylinders are located in the bottom periphery of the hopper and deliver an exact volume product through the operation of a cam-actuated piston. Many manufacturers fill the outage of the can with nitrogen to improve the keeping quality of the product by excluding oxygen from the package.

When filling bulk packages, it is customary to fill from the ''B'' unit directly into the package through an extrusion valve with the package resting on a scale.

In the case of margarine a very high percentage is packed in quarter-pound prints individually wrapped and placed four to a carton. The machine for accomplishing this involves twin screws which force the product into the measuring and forming chamber, from which it is removed and wrapped and automatically packaged four to a carton which may or may not be over-wrapped with paper, foil, or cellophane. In the last few years there have been many improvements in the packing of margarine for protection of the product and for consumer eye-appeal.

There have been no fundamental changes in the process of solidifying and plasticizing edible fat products in the past few years. Rather, product improvement has come from other processing steps, such as bleaching, hydrogenation, interesterification, deodorization, and improved methods of control.

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Fat-Splitting

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FAT-SPLITTING OR HYDROLYSIS is the term applied to the operation in which a fat or oil is reacted with water to form glycerine and fatty acid. The splitting process is important commercially because of the extensive use of fatty acids in preparing soaps, synthetic detergents, plasticizers, coatings, greases, and many miscellaneous organic derivatives. Although in soapmaking and certain other uses either fats or fatty acids can be used for the same purpose, the initial conversion of fats to fatty acids has the advantage of allowing the upgrading of poor stocks by distillation. Various physical separations of the fatty acids can also be carried out to give special properties to the products made from them.

Hydrolysis Reaction

Hydrolysis is a reversible reaction which will approach completion only if a large excess of water is used or if one of the products can be removed from the reaction mixture. In certain continuous processes the glycerine is removed, and a high degree of splitting is obtained. In batch splitting however the extent of hydrolysis depends only on the ratio of water to oil charged to the reaction vessel. This is illustrated in Figure 1 (9), where a low glycerine concentration corresponding to a high water/oil ratio gives almost complete split, and a high glycerine concentration corresponding to a low water/oil ratio gives appreciably less than complete hydrolysis.

The splitting of triglycerides has been found to proceed in a stepwise manner, with di- and monoglycerides being formed successively in the course of the reaction.

Evidence of this is given by the experiments of Mills and McClain (5), in which tallow and coconut oil were split and the combined glycerine content of the unsplit portion of the fat checked when the split was 90–99% complete. It was found for both materials that the unsplit neutral fat contained an appreciably higher percentage of combined glycerine than the original feed. This could only be caused by the presence of a considerable amount of mono- and diglycerides. The fact that the percentage of glycerine in the unsplit fat was constant in the range of 90–99% split indicates that the proportions of the glycerides are constant in this range.

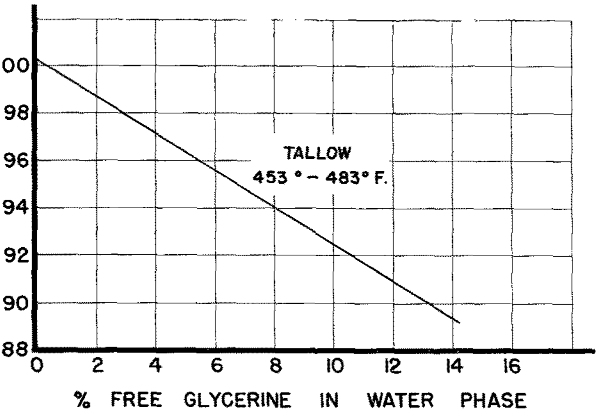

Fig. 1. *Completeness of hydrolysis vs. glycerine in sweetwater.*

Since fat-splitting involves a reaction between oil and water phases, there has been considerable question in the past as to whether it is a surface reaction or a homogeneous reaction. It was formerly believed to be a surface reaction in which emulsification of the oil and water raised the reaction rate by increasing the contact surface between the two phases. More recent work by Lascaray (5, 6) however has shown fat-splitting to be a homogeneous reaction taking place in the oil phase as a result of the water dissolving in the fatty material.

It has been observed in batch-splitting operations that there is an initial induction period during which the reaction rate is low, followed by a period of rapid reaction, and finally ending in a reduced rate period when the reaction approaches equilibrium. Lascaray has shown that, for the splitting to proceed at a satisfactory rate, water must dissolve in the oil phase. He has also shown that at 212°F. water is only sparingly soluble in neutral fat, but as the free fatty acid content increases, the water solubility increases until it is 4–5 times greater than it was originally. The low rate period at the start of a batch-splitting operation results from a low concentration of water dissolved in the oil phase. As some free fatty acid forms, the solubility of the water increases, and the rate follows accordingly. This indicates that the addition of free fatty acid to the initial reaction mixture can be used to eliminate the induction period. A low grade feed material will, of course, already contain enough free fatty acid to eliminate the possibility of a long induction period.

Considering the effect of catalysts on the reaction rate, Lascaray has indicated that both acid and basic catalysts act by increasing the solubility of water in the oil phase. In the case of basic autoclave splitting he has compiled the following list of relative catalyst activities, each referred to the splitting rate with water alone. In the splitting operation these oxides and hydroxides react with fatty acids to form soaps which are the actual catalysts.

ZnO	MgO	CaO	LiOH	NaOH	KOH	NH_4OH	H_2O
6.0	3.1	2.3	2.0	1.7	1.4	1.1	1.0

Another method for increasing the reaction rate is to increase the operating temperature. As shown in Figure 2 (9), the solubility of water in fatty acids becomes quite high as the temperature is raised above 350°F. Since the reaction rate increases with increased water solubility, a rise in temperature should give a higher rate. The curves in Figure 3 (10) show this to be so.

Figure 3 also shows that, although reaction rates are affected markedly by temperature, the final split is essentially the same in all cases. The independence of equilibrium concentration on temperature indicates that the splitting reaction has zero heat of reaction.

Summarizing the foregoing discussion, it can be said that fat-splitting is a stepwise homogeneous reaction taking place in the oil phase with the final equilibrium split depending only on the concentration of glycerine and with rate of reaction affected chiefly by catalyst and operating temperature.

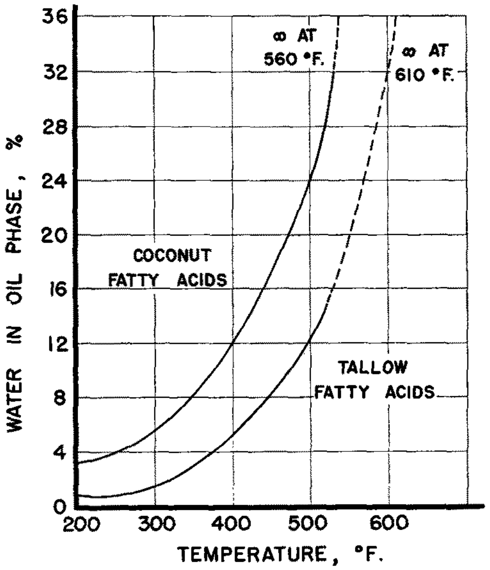

Fig. 2. Solubility of water in fatty acids.

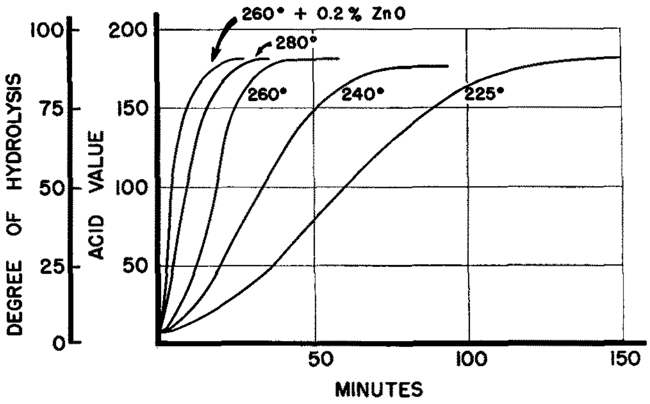

FIG. 3. Hydrolysis of beef tallow.

Fat-Splitting Processes

Fat-splitting is carried out commercially by either batch or continuous methods. In addition to the special characteristics of the individual processes which will be discussed later there are certain advantages and disadvantages common to all batch operations or all continuous operations. In comparing the two methods, the batch is generally found to have a lower first cost and be more suitable for small installations. Where relatively small amounts of a variety of fats are to be split, the batch operation would be chosen. However labor costs and operating space are high in a batch process for a given production rate. The continuous processes give uniform product quality, have low labor costs and constant low utility loads, and require a relatively small floor area. They have a higher first cost than batch processes however, require greater operating skill, and are generally more suitable for processing large quantities of a few fats where operating conditions can be held constant once on stream.

Twitchell Process. The most commonly used batch process for fat-splitting in the United States is the Twitchell process (1, 12). In this operation the fat is split by boiling with water in the presence of an alkyl-aryl sulfonic acid catalyst. The reaction is carried out in lead-lined or Monel tanks at atmospheric pressure. The tanks are usually covered to minimize air contact with the fatty acids, but there is still some oxidation with resulting color-darkening. Before Twitchell-splitting low grade fats, they are generally boiled with dilute sulfuric acid to remove albuminous material which poisons the catalyst.

In the Twitchell-splitting operation the fat is mixed with 25–50% of its weight of water, and 0.75–1.25% catalyst is added. The mixture is boiled with open steam for 20–48 hrs. and then allowed to settle for a sufficient length of time to allow separation of the glycerine solution from the fatty acids. To avoid excessive time-consumption and weak glycerine solution, it is common to split in more than one stage. In two-stage operation the glycerine solution is withdrawn when about 85% split has been reached in the first stage. Fresh water is then added in the second stage, and boiling is continued until the split is 95% complete. Since it has previously been shown that over-all split depends on the concentration of the glycerine solution in the reaction mixture, it can be seen that the two-stage process allows the production of a relatively high concentration of glycerine in the first stage where complete splitting is not desired. A weaker solution is obtained from the second stage, but this can be used as part of the water charge of a subsequent first stage batch. As many as four stages are used commercially with the glycerine solutions passing countercurrent to the oil, *i.e.,* fresh water fed to the fourth stage, weak glycerine solution from the fourth stage fed to the third stage, etc. Concentrations of glycerine solutions of 5–15% can be obtained, depending on the number of stages used and the degree of split desired.

Twitchell-splitting has the major advantage of using relatively simple and inexpensive equipment because of its operation at a moderate temperature and atmospheric pressure. Its disadvantages are that it requires a long time for the reaction to be completed, has high steam consumption, gives dark colored fatty acids, and requires the addition of and later removal of catalyst. Pretreatment of low grade stocks is usually necessary, and for all stocks operation in stages is necessary to get satisfactory split and high glycerine concentration.

Batch Autoclave Process. The autoclave process for splitting is the oldest commercial method used, originating with the Tilghman Patent (11) in 1854. At the present time it is more commonly used in Europe than in the United States. This process may be carried out either with or without catalyst.

In autoclave-splitting with catalyst (1, 7) cylindrical stainless steel reaction vessels 4–6 ft. in diameter and 20–40 ft. high are used. These have open steam agitation and are insulated to minimize steam condensation. The operation is run at about 365°F. (150 p.s.i.g.) with 2–4% of ZnO, MgO, or CaO catalyst added. It can be seen that these are the most active catalysts in Lascaray's table previously shown.

The fat and catalyst are charged to the autoclave along with water equal to 30–60% of the weight of fat. Steam is then blown through the batch at atmospheric pressure to displace all air from the vessel. The vent is then closed, and steam flow is continued until the desired operating pressure is reached. Agitation with open steam is continued, the vent being opened enough to allow a continuous flow of steam while maintaining the operating pressure. After 6–10 hours a split of 85–90% is reached. The batch is then blown to a settling tank where the glycerine solution and fatty acid are separated. The fatty acid is given a treatment with mineral acid at this time to decompose the soap formed by the catalyst and is water-washed to remove the metal salts and excess mineral acid. As with Twitchell-splitting, it is common to do autoclave-splitting in stages. Depending on the number of stages used, a glycerine solution concentration of 10–15% can be obtained with a split of 95–98%.

The catalytic autoclave process has the advantages over the Twitchell process of a shorter reaction time and, because of this as well as the absence of air, production of lighter colored fatty acids. It has the disadvantage of higher first cost because of the high pressure operation, and, as with the Twitchell Process, must be carried out in stages for best yield.

A more recent development in autoclave-splitting is the use of high temperatures and pressures with no catalyst (1). This process is carried out in stainless steel autoclaves provided with mechanical agitation. Operating at 450°F. and 425–450 p.s.i.g., rapid splitting is obtained, and there is no necessity for treating the fatty acids for removal of catalyst.

Enzyme Process. A final batch-splitting process, and one which is now of little interest commercially, is the Enzyme Process (1). The procedure is to charge to an open lead-lined tank the fat to be split, 30–40% of its weight in water, and 6% of a fermented mix of ground castor beans and water. The pH is adjusted to 5 with acid, about 0.2% of manganese sulfate is added as an activator, and the mixture is agitated to form an emulsion. The batch is held at about 95°F. for 24–48 hrs. with occasional mixing, at the end of which time a split of about 90% has been achieved. The emulsion is then broken by heat and the addition of a small amount of sulfuric acid, allowing the fatty acids to be separated.

Since this process cannot be carried out above 100°F. without sharply reducing the activity of the enzymes, it is limited to the splitting of materials which are liquid below this temperature. It also has the disadvantage of excessively long batch times, further complicated by varying activity of the ferments used.

Continuous Countercurrent Splitting. In continuous countercurrent splitting (4, 8) fat and water at elevated temperature and pressure pass through a column countercurrent to each other and react to form fatty acids and glycerine. The glycerine dissolves in the excess water and is carried out of the reaction zone, thus allowing the hydrolysis to go almost to completion. The temperature is maintained sufficiently high to give appreciable solubility of water in the oil phase, and the pressure is set high enough to prevent vaporization of the water.

The operation is carried out in a Type 316 stainless steel or Inconel column, usually about 3 ft. in diameter and 70 ft. high for a fat throughput rate of 5,000–7,500 lbs./hr. The temperature of the column is 480–500°F., and the pressure 700–725 p.s.i.g. As shown in Figure 4, the fat is introduced into the bottom of the column, and water at a rate of 0.5 lb. per pound of oil is introduced at the top. Stainless steel triplex plunger pumps are used for the two feed-streams. With an interface maintained near the bottom, the fat rises slowly up the column as the continuous phase while the water drops through it as the dispersed phase. At the bottom of the column a pool of glycerine solution or "sweetwater" collects and is discharged continuously to maintain a constant interface level. The fatty acids leave the top of the column at a rate controlled to maintain a constant pressure in the unit.

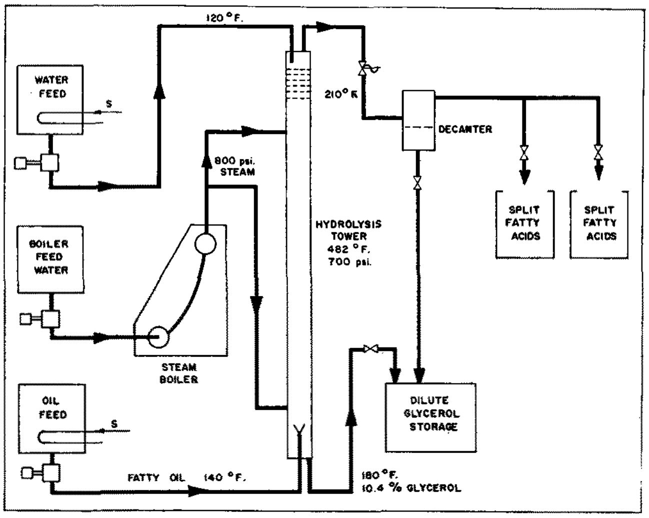

Fig. 4. Flow sheet for continuous countercurrent fat-splitting.

The hot fatty acid and sweetwater streams leaving the splitter exchange heat with the cold water and fat streams entering to carry them part way up to the operating temperature. Direct injection of 800-p.s.i.g. steam near the top and bottom of the column gives the additional heat needed to raise the temperature of the reactants to 500°F. The steam is obtained either from a high pressure boiler or from a steam compressor. The partially cooled fatty acids leaving the column still contain several per cent of dissolved moisture, and this flashes as the pressure is released with a resulting temperature drop to about 210°F. At the reduced temperature additional water separates from the fatty acids, and this is removed continuously in the decanter. The final product will contain 96–99% free fatty acid and 1% moisture. The sweetwater will have a glycerine concentration of 10–18% depending on the fat stock being split.

The capacity of a given splitter can be increased somewhat by the use of zinc oxide catalyst, but since this necessitates an additional treatment of the product for catalyst removal, it is not often done. Other refinements of the process include deaeration of fat and water feed as a precaution against darkening of the product, and the use of deionized feed-water to prevent sludge formation in the column due to insoluble soaps.

Continuous countercurrent splitting has the advantages of giving a higher degree of hydrolysis and more concentrated glycerine solution in a single operation with no catalyst than any of the other processes. Holdup time is low, amounting to only 2–3 hrs. This short exposure to high temperatures results in light colors of the fatty acids produced. The low holdup time also means that relatively small amounts of material are in process at any one time, and smaller inventories may be carried. The chief disadvantages of this process are its high first cost compared with batch processes, its high operating temperature and pressure, and its lack of suitability for a small plant handling a large number of different feed stocks. The latter objection has been overcome to some extent however with the introduction of a packaged unit capable of processing 500 lbs./hr. (2). By using the technique of displacing all fatty material from the column with water when it is desired to change feed–stocks, it is possible to change over with the production of no off-grade material and only a small loss of time.

Continuous Concurrent Splitting. Another method of continuous fat-splitting is the Eisenlohr Process (3, 7). In this process the fat and water are emulsified and passed rapidly through a long Inconel or stainless steel coil of relatively small diameter, maintaining a pressure of 2,500–3,500 p.s.i.g. while heating to 600°F. The mixture discharges into a flash chamber, where some of the water evaporates, resulting in a 35% sweetwater concentration. However because of the concurrent flow of the fat and water, a split of only 85–90% is obtained. This process has all of the advantages of a continuous operation, but it gives a lower split than the countercurrent process, has a lower throughput rate, and has the additional disadvantage of operating at a very high temperature and pressure.

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Part II of 1956 Short Course Lectures will appear in the November issue.