

Fat Splitting and Distillation

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IN the years between 1813 and 1818 a French scientist, Michel Chevreul, published a series of papers in which he showed that fats and oils were combinations of glycerol with fatty acids. Since that time, many methods of hydrolyzing them have been tried. While some of these methods never left the laboratory stage, they aided considerably in the development of the present industrial methods of fat splitting.



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Fat splitting is generally defined as the process of obtaining fatty acids from triglycerides by using water at high temperatures and high pressure or by catalyzing the action of the water at relatively low temperature with an acid or alkaline catalyst. In contrast the liberation of fatty acids by treating a fat or oil with an alkali, followed by acidulation of the soap formed is usually termed

saponification. The terminology may be somewhat confusing in that catalysts used in fat splitting are frequently called "saponifiers" and the process of fat splitting called saponification. Since the alkali saponification method is rarely used in present commercial practice, this discussion will be confined to "fat splitting" processes.

Simply expressed, fat splitting involves the addition of three mols of water to one mol of triglyceride to produce three mols of fatty acids and one of glycerol.

The exact mechanism of "fat splitting" involves step-wise reactions or stages, in which the fatty acid radicals are removed one at a time. During the course of fat splitting there exist monoglycerides, diglycerides, and triglycerides in equilibrium with fatty acids, water, and glycerol. The main objective in fat splitting is to obtain a maximum of fatty acids and glycerol. Since the reaction is reversible, it is necessary to remove either the glycerol or the fatty acids to shift the equilibrium. Fundamentally all methods of fat splitting use this principle and differ only in the methods of application. These methods may be classified as acid splitting, basic splitting, continuous high temperature splitting, and enzymatic splitting.

All these methods employ water as the hydrolytic agent. They differ in the means of obtaining an intimate contact of the water with the fat or oil, in the exact mechanism of the hydrolysis, and in the physical method of removing the glycerol and fatty acids.

Acid Splitting

The acid splitting process is one of the earliest commercial methods used in the hydrolysis of fats and oils. It is well known that dilute mineral acids effect a degree of hydrolysis of fats. However to obtain a high degree of hydrolysis intimate contact between

the fat and acid is necessary. In 1890 Ernst Twitchell (1) discovered and patented a method of acid splitting by the use of a catalyst which had the ability to cause intimate contact between the fat and acid water to obtain a high degree of fat splitting. This catalyst, well known as the Twitchell Reagent, is essentially a sulfonate of phenyl stearic acid. Intensive research on fat splitting reagents followed, resulting in numerous types of reagents. Out of these the reagent most used today is that patented by Petrov (2). It is a water-soluble sulfonic acid, derived from the acid refining of petroleum oils.

The Twitchell Process is a widely used method of fat splitting; simplicity of operation, relatively inexpensive equipment, and adaptability to small throughput are factors which will promote the popularity of this process for many years to come. It involves the boiling with open steam of purified fats or oils with water containing a small amount of sulphuric acid and fat splitting catalyst. In most cases the fats to be Twitchellized are acid-washed to remove or decompose foreign materials such as metal soaps, protein, etc., which may poison the catalyst. Usually acid washing consists of boiling the fat with open steam and adding from 1 to 3% of H_2SO_4 based on weight of fat. After addition of the acid, boiling is continued for approximately one hour; the spent acid is allowed to settle and is drawn off.

Then, based on the weight of the purified fat, 25 to 50% of water, 0.6 to 1.5% of splitting reagent, and 0.75 to 1.25% H_2SO_4 are added. This mixture is boiled with open steam for 12 to 15 hours at which time the hydrolysis is close to equilibrium conditions, due to the concentration of the glycerol in the water. After settling, the glycerol-water solution (commonly termed sweetwater) is drawn off, neutralized with either lime or barium hydroxide, and further treated to recover the glycerol. At this point the fatty layer will show about 80% hydrolysis. A second boil is given this fatty layer with the addition of water containing H_2SO_4 (no reagent is added), and after 5 to 10 hours the degree of hydrolysis will be as high as 95%. The sweetwater from this second boil will contain 3 to 5% glycerol and may be used as water for initial boil of additional fat. Additional stages or boils may be made in order to achieve a high degree of hydrolysis. However sweetwater from these additional stages contains such small quantities of glycerol that recovery is difficult and impractical.

The fatty acids obtained from acid splitting are dark in color and contain the fat splitting reagent. Consequently further purification, usually by distillation, is necessary to obtain high quality, light-colored fatty acids. The boiling tanks are usually lead lined or of monel construction and fitted with covers to minimize air contact during splitting operations.

Basic Process

The practice of batch autoclave splitting of fats, using an alkaline catalyst (basic process), is mainly confined to European countries. The batch autoclaves, usually of iron construction, operate at about 150 psi. As catalyst 2 to 3% of lime, magnesia, or zinc oxide is

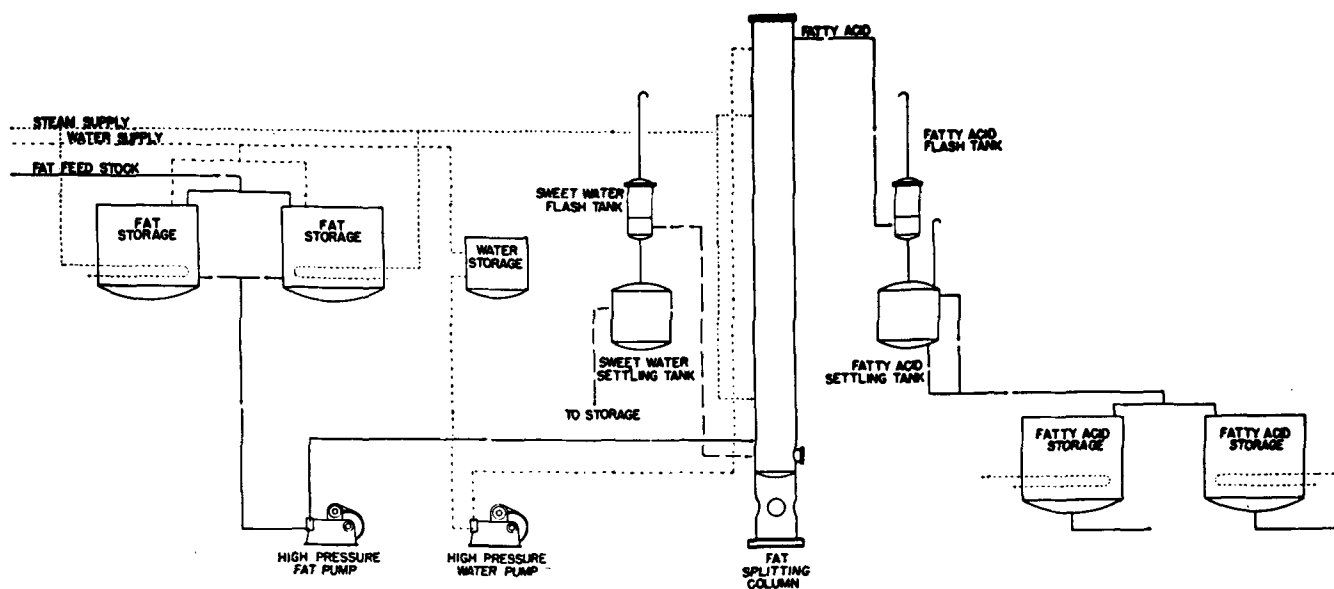


FIG. 1. Continuous counter-current high temperature fat splitting (Colgate-Emery process).

used. Apparently the small quantity of soap formed by the action of the catalyst on the fat acts as an emulsifier, causing intimate contact of the fat and water. The autoclave is charged with fat, catalyst, and water amounting to 40 to 60% based on fat weight. Steam is then admitted to the autoclave to raise the pressure to about 150 psi and corresponding temperature (ca. 180°C.). In 10 to 15 hours a 95% split is obtained, and the autoclave discharged to a settling tank. Sweetwater is further processed to recover the glycerol. The fatty acids are treated with a mineral acid, usually H_2SO_4 to decompose the soaps formed by the catalyst. The fatty acids obtained are somewhat lighter in color than those from acid splitting. It is also possible to use higher pressures on the order of 450 psi with proper autoclave construction. At these higher pressures catalysts may not be used although the addition of a catalyst will greatly speed up the rate of hydrolysis of the fat. Generally the autoclaves have a capacity to enable the production of about 5,000 pounds of fatty acids per day.

Continuous High Temperature Splitting

The splitting of fats and oils in the presence of water at very high temperatures (500°F. or 260°C.) and corresponding pressures was initially proposed by Tilghman in 1853. It was unfortunate that materials of construction which would withstand the high pressures and resist the corrosive action of the fatty acids at the high temperatures were not available. Nearly a century passed before this principle of splitting could be put into commercial practice. The proper design and technique of operation also had to be developed. The work of Brown (3), Ittner (4), and Mills (5), has made possible the present continuous, countercurrent high temperature splitting process. The main piece of equipment in this process is the column, which is 60 to 70 feet tall and fabricated of either Inconel or Type 316 stainless steel. These two metals fulfill the requirements of good corrosion resistance at temperatures of 500°F. and pressure of 725 psi.

The operation of a high pressure splitting unit is relatively simple. The simplified flow-sheet (Figure

1) of the Colgate-Emery Process of high temperature countercurrent splitting is typical (6). Fat or oil is introduced into the bottom of the column by a high pressure feed pump and is heated as it flows upward through the descending sweetwater. The fat is hydrolyzed as it travels upward through the column. The glycerol is removed by a descending flow of water charged into the top of the tower and flowing countercurrently to rising fatty acids. The sweetwater is let down in pressure from the bottom of the column into a flash tank. The fatty acids are discharged from the top of the column through a back pressure control valve. An ingenious method of heat exchange between the fatty acids and water requires that only a small amount of direct steam be introduced into the column to maintain 500°F. temperature. An exceptionally high degree of hydrolysis is obtained, ranging from 97 to 99%. This high degree of hydrolysis is due entirely to the countercurrent feature. Many other advantages are claimed for this method of fat splitting, notably, lower cost of operation, higher glycerol content of the sweetwater ranging from 13 to 18%, simplicity and ease of operation due to automatic controls and inherent benefits of a continuous process. The quality of the fatty acids is exceptionally good, particularly from high grade fats which can be used directly for soaps without further purification.

Enzymatic Splitting

Fat splitting by the use of enzymes has never developed into wide-spread commercial use. However it is of interest since it requires very little heat and is supposed to produce fatty acids of light color. It is reported that fat splitting as well as reconstitution of fats in the human body is due to the action of the enzyme, lipase. Enzymes for fat splitting are obtained from vegetable seeds, usually castor beans. Since fermentation action is involved, temperature control is necessary, around 30°C., which limits the process to fats melting below this temperature. Fat, together with 40% of its weight of water as inoculated with 4 to 7% of a ferment of the enzymes, is agitated into an emulsion and after about 50 hours a 90% split is

obtained. Naturally the long time involved and uncertainty of the reactivity of the enzymes have limited the popularity of this process.

Distillation

Fatty acids from the various fat splitting processes are relatively dark in color and contain impurities and unsplit glycerides. In most cases it is necessary to purify further the fatty acids by distillation which removes the fatty acids and leaves the glycerides and impurities in the residue.

Many ramifications of methods of fatty acid distillation and the design of fatty acid stills exist, but fundamentally they all involve the same basic considerations. Distillation of fatty acids may be either batch or continuous, at atmospheric pressure or under reduced pressure; it may be simple distillation involving only purification of the mixed fatty acids or fractional distillation consisting of both purification and separation of the fatty acids according to their chain length.

Much has been written about the basic principles of distillation, and considerable data have been published relative to the physical properties of fatty acids, especially specific heats and vapor pressures. A comprehensive discussion of the theoretical aspects of fatty acid distillation is beyond the scope of this paper. Typical methods of fatty acid distillation will be described.

Batch type distillation at atmospheric pressure is probably the oldest of commercial processes and is still employed in certain foreign countries. In this method a direct fired still pot (usually of iron construction), fitted with a steam sparger, is charged with fatty acids and heated to 500° to 600°F. while superheated steam at 300°F. is blown through the fatty acids. The ratio of steam to fatty acid vapor is approximately 5 to 1. The steam and fatty acid vapors are condensed separately, but, due to the large quantity of steam used, appreciable amounts of fatty acids are entrained with the steam condensate. The economy of this type of distillation is poor because of the excessive amounts of steam required.

Prolonged heating of fatty acids at high temperatures results in considerable decarboxylation and polymerization with consequent large amounts of residue and pitch. Other changes occur in the structure of the unsaturated acids which may not be desirable. Typical operations of atmospheric batch distillation on tallow fatty acids of about 95% hydrolysis yield 15 to 20% entrained fatty acids and 10 to 15% residue. Resplitting of the residue and distillation yields low quality fatty acids and a final pitch residue of 5 to 8%.

Improvements in batch fatty acid distillation were brought about by the use of vacuum equipment which permitted the distillation of the fatty acids under reduced pressure at lower temperatures and reduced steam consumption, resulting in lower yields of residues. Improvements in still pot design, condensers, and use of corrosion resistant materials of construction did much to increase the yields of good quality distilled fatty acids. Nevertheless batch distillation has the disadvantage of holding the fatty acids for a prolonged time at high temperatures. It is essential that the time of heating fatty acids, particularly those of high polyunsaturated acid content, be as short as possible to minimize decomposition and polymeriza-

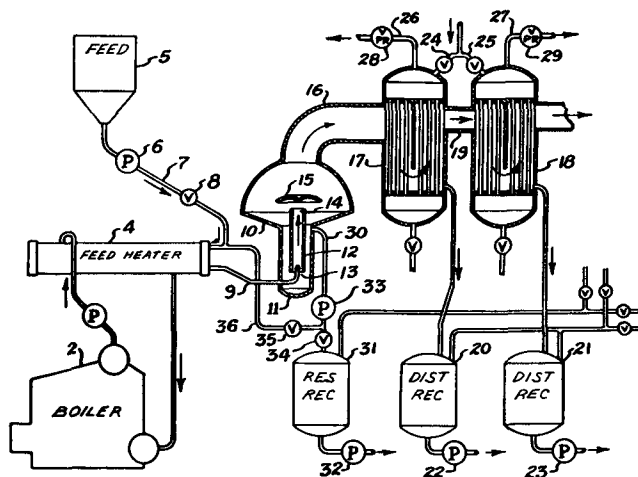


FIG. 2. Continuous distillation (Mills).

tion. Obviously the solution is the use of continuous distillation methods. In continuous distillation the fatty acids are continuously dried, preheated, and fed to a distillation chamber or column which is under reduced pressure. Generally heat is also supplied to the column. The fatty acids are vaporized quickly. The vapors pass through scrubbers or entrainment separators and condense. Superheated steam may be injected to assist vaporization of the fatty acids. Condensed fatty acids and residue are continuously removed. Vacuum is normally supplied by a barometric condenser backed up with steam ejectors or mechanical vacuum pumps.

Probably the first fatty acid still employing continuous distillation was constructed by E. Wecker (7). In this still preheated feed flows through a series of rectangular chambers, from which the fatty acids are vaporized by heating the chambers underneath with gas or oil burners. The flow of feed through these chambers may be either in series or parallel or combinations thereof. Superheated steam is injected into the chambers to assist the vaporization of the fatty acids. The vapors are led to a main vapor pipe header, condensed in a water cooled condenser, and continuously removed. The steam passes on to a barometric condenser, and the non-condensable gases are removed by a vacuum pump. Vacuum on the still is maintained at 30 to 35 mm. pressure, dependent on temperature of the water in the barometric condenser. Temperatures in the still chambers range from 385° to 500°F. Residence time of the fatty acids is about 30 minutes. The residue is continuously removed from the final distillation chamber into a receiver, which is periodically emptied.

In stills of later design the trend has been towards the use of lower pressures, lower residence time, indirect heating with diphenyl oxide, and the use of vertical still columns fitted with various types of plates or with bubble cap trays. Corrosion resistant materials of construction are used extensively. Other factors in design of heat exchangers contribute to economy of operation while efficient use of entrainment separators, condensers, and automatic controls have improved the quality of the distilled fatty acids. Rates of feed range from 1,000 to 5,000 lbs./hr.

Typical advances in design is the modified Lurgi fatty acid still. Originally a batch type still, modifications (Figure 2) converted it to a flash type contin-

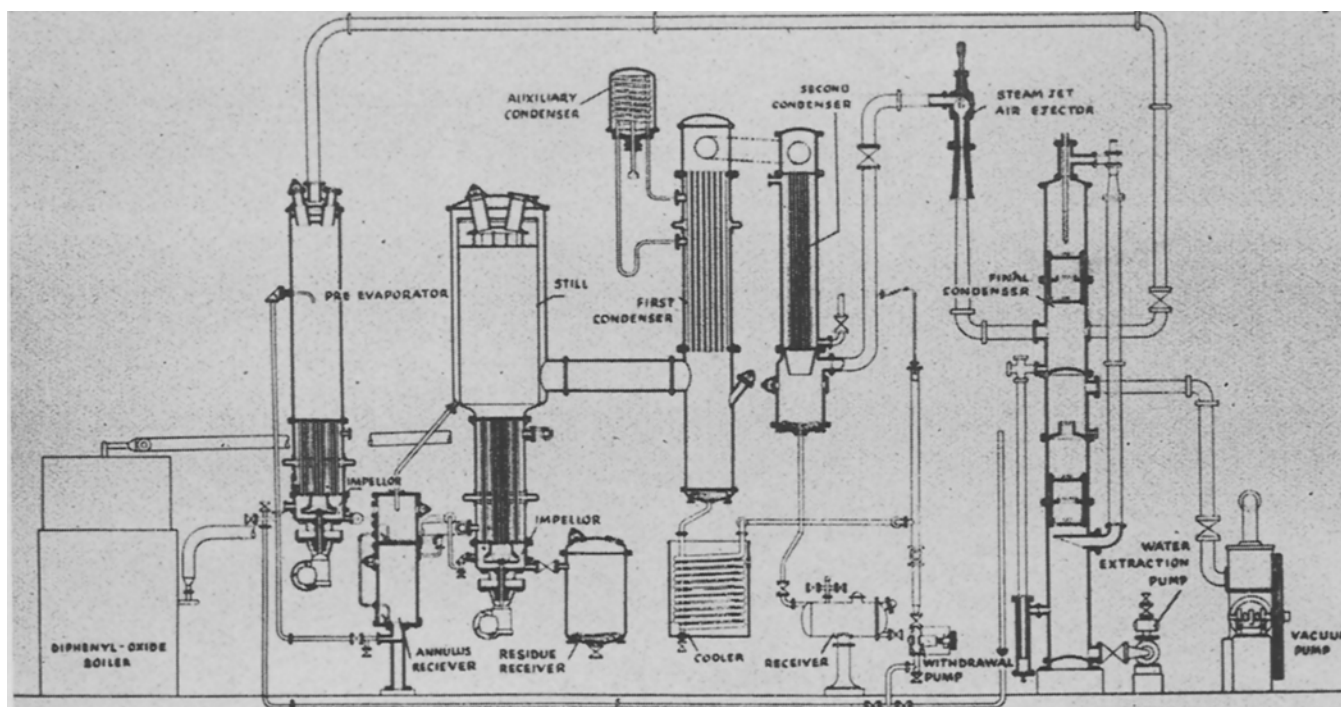


FIG. 3. Continuous distillation (Scott)

uous still (8, 9). Flash distillation involves heating the feed stock to a sufficiently high temperature to provide practically all of the heat of vaporization to the fatty acids before they are fed to the distilling chamber. In this modification vacuum on the still is maintained between 1 to 3 mm. Rapid preheating and almost instantaneous vaporization gives shorter residence time with resulting lower amounts of fatty acid decomposition products. Suitable baffles are provided in the still chamber onto which the preheated fatty acids impinge. Mechanical traps or separators are installed to minimize entrainment since violent action of the fatty acids occur in the still chamber. Condensation of the fatty acid vapors may be by water injection or conventional water cooled tubular condensers.

Other types of continuous stills utilizing high vacuum and vertical column still chambers are the Scott Patent Still (10) and one patented by Goranflo (11).

The Scott Still (Figure 3) uses forced circulation tubular evaporators in both a preheater and the main still columns. In the preheater or pre-evaporator fatty acids are dried, heated to 150°C., and fed continuously to the main still, maintained under a pressure of 3 to 5 mm. of Hg. Heat is supplied by a diphenyl oxide boiler. Mechanical impellers circulate fatty acids through the tubes in the lower part of the preheater and still. The still contains an internal hood, which serves as an entrainment separator. Two condensers are provided; the main portion of the fatty acids is condensed in the "hot" condenser. Coloring matter and low boiling fatty acids are condensed in the cold condenser. Vacuum is maintained on the system by a mechanical pump backed up by a steam ejector. No live steam is injected into the system. Distilled fatty acids and residue are removed periodically from the receivers.

In the Goranflo still (Figure 4) use is made of a vertical still column fitted with bubble cap trays. Fatty acid feed is preheated rapidly both by heat

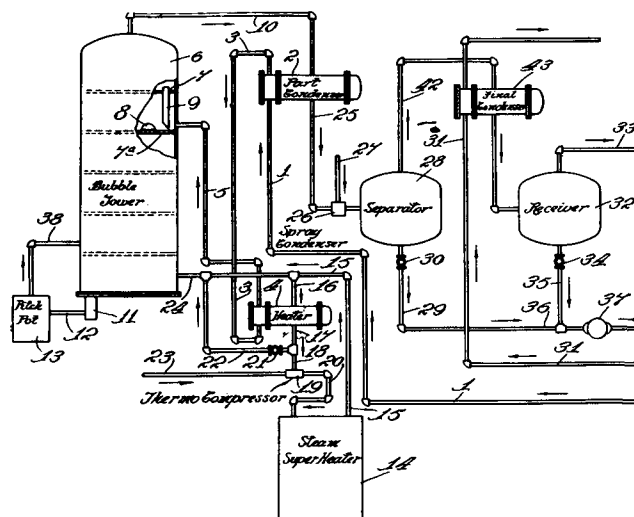


FIG. 4. Continuous distillation (Goranflo).

exchange with condensing fatty acid vapors and by preheater to 475° to 500°F. and flashed into the column on one of the upper trays. Superheated steam at 750°F. is introduced at the bottom of the column. The fatty acid vapors, often being partially condensed in the raw feed exchanger, are completely condensed in a spray condenser by water injection. The remaining condensing system after fatty acids are separated is of the conventional barometric condenser and steam ejector, which maintains a vacuum of 26 to 28 inches. Advantage is claimed for the use of the bubble cap trays in that they serve as efficient scrubbers of the fatty acid vapors to give a high quality distillate.

More recently a new improved type of fatty acid still using bubble cap trays, individually heated by Dowtherm vapors, has been described by Berger (12), of Wurster and Sanger Inc. (Figure 5). This unique

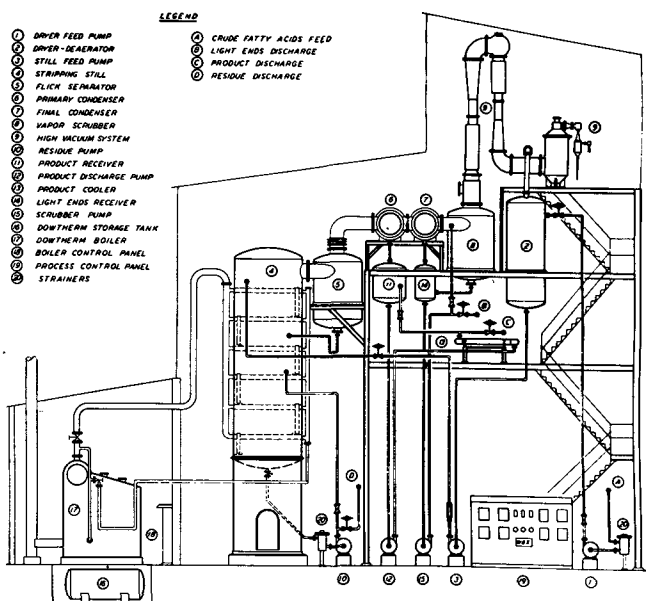


Fig. 5. Continuous distillation (Wurster and Sanger).

method of heating the trays permits the vaporization of the fatty acids in a very short time, eliminating high preheating temperatures. Due to the very short residence time of the fatty acids in the still, high yields of distillate are obtained. Fatty acids are dried

and deaerated at 110° to 200° F. under 26" to 28" Hg. and fed to the column. The column is maintained under vacuum of 5 mm. Hg. A Flick centrifugal separator reduces the amount of entrainment to a minimum. Tube and shell type condensers are used to condense the fatty acid vapors. The vapors leaving the final condenser consist of stripping steam, non-condensable gases, and some fatty acid vapors that are subjected to a wet scrubber in which a spray of fatty acids scrub these vapors, giving practically complete removal of fatty acids. Vacuum is supplied by a barometric condenser and steam jets.

Instrumentation and automatic control on this still aid in the ease and economy of operation. Capacities are from 2,500 to 5,000 lbs./hr. Yield of 96% distillate of light color from processing tallow fatty acids is reported.

The use of the vertical distilling column fitted with bubble cap trays in fatty acid distillation marked the way for development of this design for the fractional distillation of fatty acids. Fractional distillation is used to separate saturated fatty acids of different chain length. It is most effective when used to separate fatty acids of four to six carbon atoms difference in chain length. Probably its most effective use is in the fractional distillation of coconut oil fatty acids.

Armour and Company introduced in this country the process of fractional distillation of fatty acids. Plant design (Figure 6) was by the Foster Wheeler

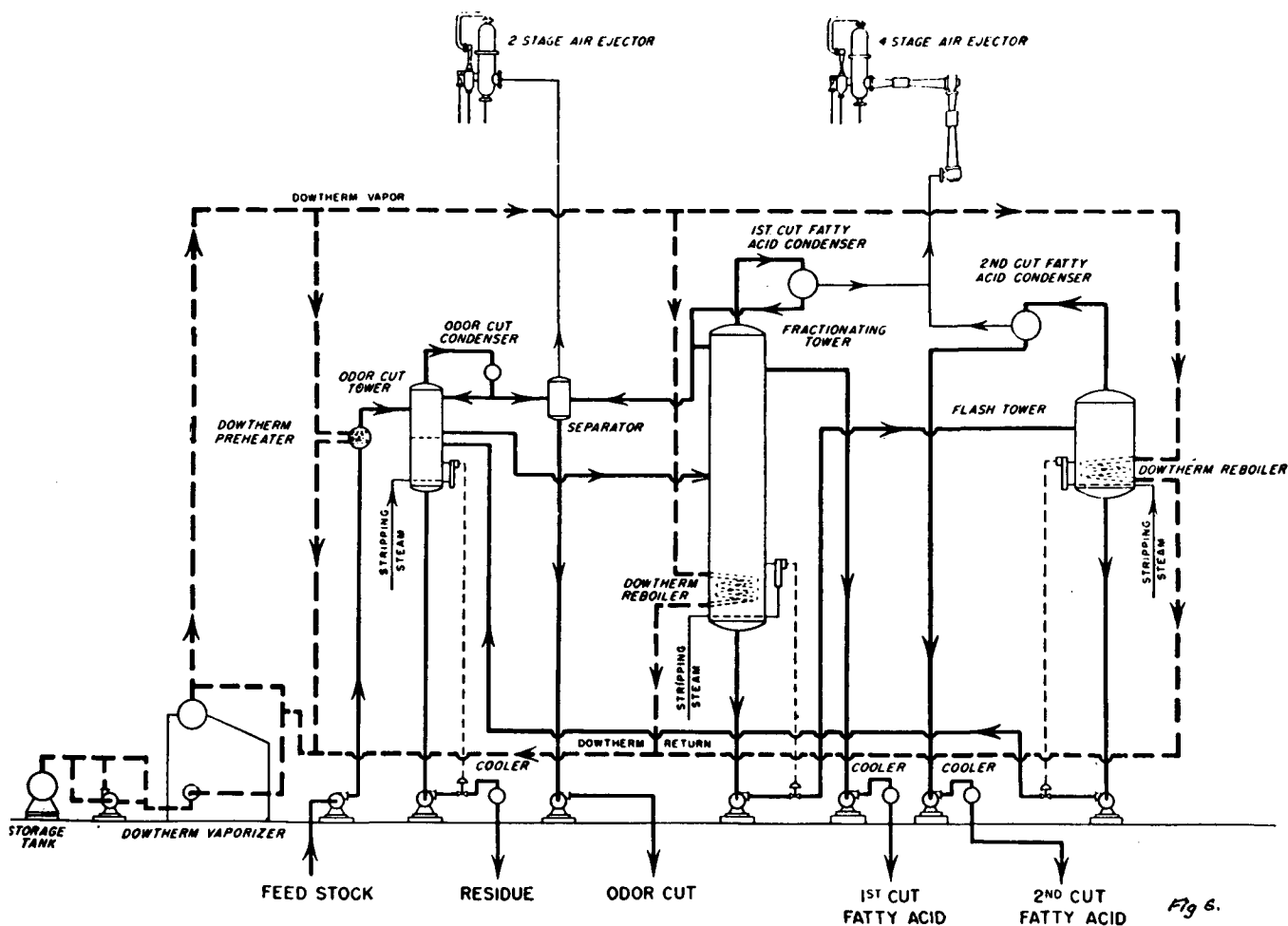


Fig. 6. Continuous fractional distillation (Foster Wheeler).

Corporation (13). This method has been described many times in the literature (14, 15), and results obtained on various fatty acid feed stocks have been widely published. Fundamentally, fractional distillation of fatty acids is carried out in the same manner as continuous simple distillation. The design of the main distilling column differs from simple distillation columns in that it is fitted with a plurality of bubble cap trays and means for removal of side streams of fatty acids and return of part of these streams as reflux. Pre-evaporator column and final stripping column are designed to remove odor cuts and residue from the system. Conventional condensers and vacuum systems are used.

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Commercial Uses of Fatty Acids

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THE total production of fatty acids in the United States has materially increased during the past decade. In 1941 approximately 225 million pounds were produced whereas in 1951 this amount increased to more than 400 million pounds. These figures do not include tall oil production, which has grown to be a very important factor in fatty acid uses, as indicated by the production of 90 million pounds of refined tall oil in 1948 and more than 141 million pounds in 1951. Production figures on refined tall oil are not available prior to 1948. This substantial increase in total fatty acid production is due to the development of a great many new uses as well as to a general increase in industrial production of established products in which fatty acids are used.



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The principal end-uses of fatty acids and fatty acid derivatives can be classified as follows: Soaps and synthetic organic detergents; Rubber compounding; Synthetic rubber polymerization; Paints, varnishes, and surface coatings; Plastics and plastic fabrication; Lubricating greases; Lubricating oils and oil additives; Cleaning compounds and polishes; Metal working and treating; Textile chemicals; Cosmetics and toiletries; Insecticides, disinfectants, and germicides; Candles; Paper and paper products; Inks and crayons; Ore flotation; Metallic soaps; and Food products.

These classifications are significant in that they emphasize the great diversification of industries and end-uses of products in which fatty acids are employed. There are few fields of manufacture or technology today which do not use fatty acids or their derivatives in one form or another.

Commercially produced fatty acids today are derived from naturally occurring animal, vegetable, and

marine fats and oils. The majority of these raw materials occur in nature as complex mixtures of triglycerides, other esters, and alcohols. Some of the more common fats and oils used are beef tallow, pork greases, cottonseed, soya, coconut, palm, palm kernel, linseed, olive, menhaden, sardine, sperm, herring, and tall oils. Tall oil, of course, is not a true "oil" since it is actually a mixture of fatty acids and rosin acids, not occurring as a triglyceride. Both crude fats and oils and the "foots" from edible oil refining are used to produce the finished fatty acids.

The first step in fatty acid manufacture is the hydrolysis of the oils. This process produces crude fatty acids with glycerine as a by-product. The four most common methods are (1) autoclave, (2) Twitchellizing, (3) saponification with caustic followed by acidulation, and (4) high pressure continuous splitting. Although all four methods are still employed the trend is toward the last of these.

The next step is some form of purification of the crude fatty acid, usually a total distillation, which Although all four methods are still employed, the trend is toward the last of these.

By the preliminary steps of hydrolysis of the oils and purification of the acids, usually by distillation, mixed fatty acids having the composition of the original oil or fat are produced, which are suitable for many uses. To obtain properties required for other specific end-uses, separation into component fatty acids, or blends of component fatty acids having similar properties, is necessary. There is a trend in the fatty acid industry in the direction of producing relatively pure acids of each kind, and, as evidence of this, there are a number of fatty acids of 90-95% purity available commercially.

In order to provide "tailor-made" fatty acids which are more suitable for certain specific end-uses than the mixed fatty acids, further mechanical and chemical processing of the distilled mixed acids is necessary. Space will not permit a full discussion of these operations although, I believe, brief mention of some of the more important processes is necessary for a better understanding of the many types of commercial fatty acids and their end-uses.