Lectures of the 1956 Short Course on Unit Processes in the Fatty Oil, Soap, and Detergent Industries

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Part II

Distillation of Fatty Acid

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PURIFICATION OF FATTY ACID by distillation has been practised for a hundred years and is still the most common and most efficient means of producing high purity fatty acids. A large amount of technical data, patent and general literature has been published, and a general paper on this subject can do little more than summarize the present state of the industry and list a few of its many problems.

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Raw materials available to the fatty acid processor range from prime oils of animal, vegetable, and marine origin down through all the by-products which are produced during the processing of these oils. Because of this wide selection of raw material a great number of pretreatment methods have been developed to produce a suitable distillation feed stock. Although it will be impossible to deal with this phase of the work in any detail, mention must be made of the major steps required to produce feed for distillation. Most stocks are mixtures of fatty acids, glycerides, and variable amounts of impurities. Usually the first processing step is hydrolysis to free the fatty acid from the glycerol radical. The degree of hydrolysis is important as any mono-, di-, or triglyceride or even free glycerol left in the fatty acid prior to distillation will result in more still residue.

Several pretreatment steps, other than the actual cleavage of fatty acid from glycerol, are important and have a direct bearing on the quality of distillate. Chief among these is acid washing. Low grade stock usually contains protenacious matter and iron, calcium, and sodium soaps. Acid washing with sulphuric acid is necessary to split these metallic soaps because their presence reduces the yields by remaining with the still residue, and in certain instances they act as catalysts producing polymers, high boiling ketones, and the like. Sulphuric acid removes protenacious matter, which if allowed to remain in the feed stock will cause foaming in the still and contamination of the distillate with unsaponifiable matter. Acid washing must be performed carefully, using the proper temperature and proper concentration of acid, otherwise sulphonation of the stock will take place, causing high losses and greater yields of pitch. After

acid washing it is necessary to wash with water to remove residual mineral acid.

The drying and deaerating of feed stock is desirable for best results. In special cases it may be desirable to refine, bleach, and hydrogenate stock prior to distillation.

The selection of the type of still and the method of operation depend upon the raw material and the type of product desired. If only a decolorizing step is necessary, one that removes the unhydrolyzed oil, polymerized products, and high-boiling color bodies, then a simple distillation is all that is required.

If considerable amounts of odor bodies, low-boiling unsaponifiable matter, and compounds which cause color reversion are present, then some means of fractionally concentrating these low boilers, such as a fractionating still or one equipped for partial condensation, is required. If the component acids must be separated from each other, then an efficient fractionating still is required.

The naturally occurring fatty acids are straight chain organic acids, varying in chain length from C_6 to C_{24} with the further restriction that only the even ones are present in appreciable amounts. Inspection of their vapor pressures shows that the addition of two carbon atoms results in a substantial increase of boiling point, making it possible to separate them by fractional distillation.

Distillation of fatty acid is complicated because of the high temperatures involved, together with the fact that at these temperatures fatty acids are thermally unstable. If fatty acid is subjected to high temperatures, say above 225°F. for increasingly longer periods of time, they decompose. Usually the first step is one of anhydride formation with the loss of one mol of water for two mols of fatty acid. At higher temperatures ketones and hydrocarbons are formed with the loss of CO_2. When decarboxylation occurs, some unsaturated hydrocarbons are formed. At still higher temperatures the carbon chain may break and the lower boiling fragments are highly unsaturated and correspondingly very unstable. Unsaturated fatty acid, such as linoleic acid, first condenses to form a dimer, then more complex polymerization reactions take place, causing higher yields of pitch.

Because of thermal instability it is necessary to design for about 250°C. maximum temperature. Other physical properties of fatty acids that must be known are the latent heat, heat capacity, and specific gravity of the liquid and vapor.

In early years the stills were operated at atmospheric pressure, and, to maintain pot temperatures of 250°C., large amounts of injected steam were necessary, readily calculated from the vapor pressure at 250°C. In the case of stearic acid this is 23 mm. Hg., and a simple calculation will determine that, for each pound of stearic acid vaporized, approximately 2.5 lbs. of steam will be required.

Reduction in pressure results in a reduction of injected steam. At 35 mm. Hg. we find that, instead of 2.5 lbs. of steam for each pound of fatty acid distilled, only .04 lb. of steam is required. In actual practice the steam use is somewhat greater than the theoretical amount because of the efficiency of the mixing.

As distillation techniques improved and more efficient air pumps were built, the operating pressures were reduced until today most of the fatty acid stills operate at pressures of between 5 and 50 mm. Hg. absolute. Even though very low pressures are obtainable with modern, efficient air pumps, it is still desirable to use some injected steam because the presence of a small amount of water helps retard anhydride formation.

When stills supplied with injected steam are operated at pressures lower than the vapor pressure of the available cooling water, it is necessary to provide a steam compressor in addition to the ordinary air pump.

The fatty acids stills which are in general use today may be classified into three general types: semicontinuous batch type, continuous simple distillation, and continuous fractionating type. The first is the oldest type, and typical examples are the old classical Garrigne still, which is still used in limited operation today, and the Scott still, made in England and in use chiefly in Europe.

The second class is rapidly replacing the semicontinuous. This is a truly continuous still, with constant feed and constant withdrawal of distillate and residue. Stills of this type are made by many manufacturers, and I shall discuss the horizontal type, a Dowtherm-heated tray type, and several types of German design.

Wurster and Sanger Dowtherm-Heated Tray Type. This still is of the true continuous type in that pitch is stripped and withdrawn continuously. A novel feature is the Dowtherm-heated plates. As the feed descends through the column, it is met with a countercurrent flow of superheated steam, and the heat for vaporization is supplied as required by the heated plates. The heated Dowtherm plates form an efficient means of stripping the volatile fatty acid from the pitch and at the same time prevent the high-boiling impurities from contaminating the distillate. Distillate is collected in two separate condensing systems. The first or hot condenser condenses the main portion of the distillate while the final "cold" condenser collects the final traces, which in general amount to about 5% of the feed. This 5% is usually of inferior quality because it contains the low-boiling unsaponifiable matter, which is the main contributor to bad

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odor, bad color, and instability if allowed to remain with the main distillate stream.

Foster Wheeler Horizontal Type. This has a horizontal still body, divided into two compartments. Both compartments are heated by horizontal tube bundles having condensing Dowtherm vapor inside the tubes. The chamber is equipped with a tight baffle to keep the vapors separate, but the liquid can flow under a weir from the primary heating coil to the main heating coil. Both vapor spaces are provided with surface condensers, a common thermocompressor, barometric condenser, and air pump.

The feed stock enters the first chamber, where it is brought up to distillation temperature of approximately 400°F. Heating removes air, moisture, and the low-boiling impurities. The stripped stock now passes under the weir into the distillation compartment, where the main distillate fraction is removed. The residue is stripped of its volatile matter as it flows along the heater trough and is removed at the far end through an overflow pipe. Pressure in the system is maintained at about 10 mm. Hg. by means of a thermocompressor.

Foreign Types. Of German design, the Wecker still has been, and still is, in considerable use today and consists of a rectangular distillation compartment. The actual vaporization is conducted in a series of troughs, which are built on the flat bottom of the still. These troughs conduct the fatty acid over a long continuous path. Heating can be done by direct heat applied to the bottom of the still or through Dowtherm or high pressure steam coils placed in the troughs themselves. Injected steam can also be supplied by coils placed in the bottom of the trough. The still is equipped with the usual "hot" and "cold" condensers, thermocompressor, barometric condenser, and air pumps.

Absolute pressure of 5 to 10 mm. Hg. is applied to the still. One advantage lies in the fact that only a very small depth of liquid is required over the heating surface, thereby preventing overheating. Vaporization takes place from the surface of the liquid. Another advantage lies in the long path of liquid travel from entrance point to residue discharge, resulting in efficient stripping.

The Lurgi type is another German still well known for many years both in the United States and abroad. The main feature is a central draft tube type of heater, into which the preheated liquid is fed together with steam and recycle liquid. The steam induces an upward flow of liquid against an umbrella-like baffle. The draft tube is heated with a Dowtherm jacket. The vapors flash from the outlet, and the liquid portion is recycled. The usual condensing and vacuum equipment is provided.

In the third class is the type used for separating charge stocks into component parts, such as a general fractionating still for all types of separations and another type better suited for the distillation of tall oil.

Fractionating Still. A stock, such as hydrogenated tallow fatty acids containing about 96–98% free fatty acid, is pumped to a first or pretreatment tower, which is operated under a reduced pressure of about 35 mm. Hg. and is heated at the base with internal Dowtherm heaters. Steam is injected at the base of the tower. The combination of steam and reduced pressure maintains a temperature not greater than 250°C. The flow of Dowtherm vapor to the base heater is controlled to provide sufficient reflux to yield the desired separation. When distilling tallow, the overhead product from the first tower is low-boiling impurities and small amounts of myristic acid. The stock leaving the base of No. 1 tower is pumped to No. 2 tower, which is operated at a pressure of 5 mm. Hg. at the top of the tower and about 35 mm. Hg. at the base. Here again a small amount of injected steam is necessary to minimize decomposition and aid in keeping the distillation temperature at the desired level. When distilling hardened tallow fatty acid, the overhead product from the No. 2 tower is practically pure palmitic acid. The high boiling fraction is then passed to No. 3 tower, which also operates at 5 mm. Hg. Stearic acid is removed as the distillate fraction.

Many fats may be separated into their component fatty acids by this technique. In addition to the production of pure palmitic and pure stearic acid the separation of the fatty acids of coconut oil is of major economic importance, primarily for lauric acid for synthetic detergent and alkyd resin use. With coconut oil a greater number of acids is obtained when a complete separation is made: *i.e.,* caprylic, capric, lauric, myristic, palmitic, stearic, and oleic.

Fractional distillation is used for the separation of crude tall oil into fatty acids and rosin acids. Tall oil is a by-product of the sulphate process for making Kraft paper. In this process wood chips are autoclaved with sodium hydroxide and sodium sulphide in order to free the cellulose. The rosin and fat present in the wood are formed into water-soluble sodium soaps, which are separated from the wood fiber on rotary filters and concentrated in multiple effect evaporators. As this liquor is concentrated, the sodium soaps salt out and are skimmed off and acidulated. The resultant product is crude tall oil, containing about 40 to 50% rosin acids, 40 to 50% fatty acids, chiefly linoleic acid and oleic acid, and 5 to 10% unsaponifiables, mainly sterols or sterol esters.

Tall oil is an excellent source of rosin as well as fatty acid and may become the chief source of wood rosin because of the diminishing supply of old pine stumps, the other source of wood rosin. With excellent prospects for continued availability, as well as ever increasing demand for the products, it is small wonder that more and more firms are entering the tall oil distillation field.

In general, stills for the separation of tall oil can be operated in the following manner. Crude tall oil is fed to a heater and then to a flash tower, where the non-volatile matter, sterols, and polymerized matter are removed. The vapor, consisting of fatty acid, rosin, and low-boiling impurities, passes to a distillation tower where the impurities are removed from the top zone of the main tower. The main fatty acid fraction is removed from a zone near the top and on the first distillation usually contains 2–5% rosin acids and about 3% unsaponifiables. This fraction can be refractionated in the same tower at a later time, or it can be handled simultaneously in a separate tower. Upon refractionation an excellent grade of alkyd resin type of fatty acid with about 1% or less of rosin acid and a Gardner color of 4 to 6 is obtained. The rosin acid descends through the tower and is drawn off at the base. Reflux heat for the fractionation is usually furnished by the Dowtherm-heated

reboiler. To maintain the desired temperature of the boiling rosin at the base of the tower, one practice is to inject a rather substantial quantity of steam as well as maintain a reduced pressure. The steam serves the additional function of stripping the fatty acids out of the rosin (1–3%). Tall oil rosin is light in color and low in unsaponifiables. The fatty acid fraction is chiefly oleic, 46%, and linoleic, 48%, with about 5% palmitic. In the usual fractionation procedure much of the palmitic acid is removed with the unsaponifiable matter.

Most of the new stills are designed to separate rosin and fatty acid; however a number of stills now in operation produce over-all distilled tall oil. These stills are usually not as desirable as the complete separation type because both the rosin and fatty acids command premium prices only when separated as completely as possible.

General Equipment Common to All Stills. Still development has been aided greatly by the availability of corrosion-resistant metals and alloys. Stainless steels, nickel and silicon, cast iron, high nickel alloys of many types, copper and bronze, and aluminum all resist the action of fatty acids to various degrees. None of these materials however can be considered a universal solution to the corrosion problem, and great care must be used in selection for a specific purpose.

Stainless steels without molybdenum are not recommended for temperatures above 400°F. We prefer the molybdenum content of type 316 stainless steel to be about 2.5% for general high temperature distillation service. Type 317, Duramet 20, and some of the Hastelloys are exceptionally resistant and find special uses where the added expense can be justified. Copper and its alloys are more resistant than stainless steels in locations where mineral acid is present along with fatty acid. The objection to copper stems from the green discoloration when air and/or moisture is present together with fatty acid. Aluminum is excellent for lower temperature service because its salts are white and trace metal does not induce rancidity as Fe, Cu, and Ni are likely to do.

The preferred method for heating fatty acid stills is by an indirect means, usually Dowtherm vapor, although high pressure steam is also very efficient. Its only disadvantage is the high pressure since usually 900 to 1,000 psig. are required.

Dowtherm vapor is supplied at pressures from 0 to 30 psig., in some instances even higher. It is preferable to work at the lowest pressures and temperature. Naturally the expense of stainless steel heating-surface is a determining factor as to the practical mean temperature difference. From 50 to 100°F. is a reasonable figure. Dowtherm vapor should be generated as close as possible to the requirements of the process because the higher the boiler temperature, the more the decomposition and loss of Dowtherm. Dowtherm generated at high pressure and used at much lower pressure carries much of its heat as superheat, and higher metal temperature than necessary will prevail in parts of heaters where large reduction of pressure takes place. Submerged heaters tend to remain cleaner than those which are exposed. Dry hot surfaces tend to coke badly.

In the design of condenser equipment consideration must be given to the fact that many of the saturated fatty acids have high melting points and that cold condensing surfaces will foul with solidified fatty acid. We design for cooling water to be at temperatures higher than the highest melting point of fatty acid, which will be in contact with the cooling surface. When fatty acid is inside the tube, it is well to use a tube size which permits cleaning.

All parts coming in contact with fatty acid vapor or liquid, of course, must be made of corrosion-resistant material, including those parts subjected to water and steam that have a possibility of having fatty acid contamination. Vapor pipes leaving the condensers are best made of stainless steel and the castings for thermocompressor of a nickel cast iron. Barometric condensers, because of the large volumes of water handled, can be made of steel or cast iron.

Valves for process are usually stainless steel with Teflon packing. Pumps are usually of the centrifugal type and for still work are rather special because of the high temperatures involved. They are fitted with water-cooled glands. We prefer pumps operating at 1,750 r.p.m. Mechanical seals are proving to be very satisfactory.

Instrumentation usually causes little trouble, but the high melting point of the saturated fatty acids must be considered and steam tracing and insulation provided for. Flow instruments are best selected from the rotameter type because orifice meters cause trouble due to moisture settling out in the orifice lines or the orifice lines themselves solidifying.

Pipe-lines must be steam-traced and insulated. No method of tracing has proved to be perfect, and it is costly and difficult to install and maintain, but it must be done if trouble-free operation is desired. We use ⅜-in. copper tubing, first wired to pipe, then wrapped with aluminum foil before applying insulation. On long straight lines ½-in. steel pipe can be spot-welded to the pipe-line at intervals. In cases of very high melting materials, such as tall oil rosin, ordinary tracing may not prove sufficient and completely jacketed lines and valves are required.

A few words regarding the handling and storage of the finished distillates may be worthwhile. It is no easy task to produce distillates of good color and odor, and to keep them in this condition presents almost as many problems as making them.

Pumping and transfer lines should be of aluminum or stainless steel. While steam tracing may be necessary, it is not desirable to keep them too hot because the stock remaining in an unused heated line is sure to degenerate in quality.

Aluminum storage tanks are excellent for finished fatty acids. We prefer closed tanks, properly insulated, and heating preferably by indirect means. If coils are placed inside tanks, very low temperature differences should prevail between the heating medium and the maximum stock temperature required.

A further refinement is the application of an atmosphere of N_2 above the liquid. This is especially important for unsaturated stocks. In tanks that are in fairly regular service it is far better to maintain the acids at a temperature slightly above its melting point rather than alternately melt and allow to solidify.

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