Lectures of the 1958 Short Course on Syndets and Soaps

conducted by

The American Oil Chemists' Society

at the

Princeton Inn, Princeton, N. J., July 14-18

Under the sponsorship of the Education Committee, K. F. Mattil, Chairman

Part II

Glycerine Production and Refining

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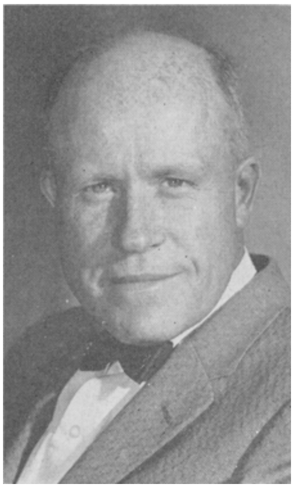
Besides being an important chemical compound, glycerine is used as a building block for other chemical syntheses. The proper chemical term for the compound is "glycerol," but the name glycerine is so firmly embedded in common usage that it is used to refer to all commercial products of any grade or purity. As an example of using both terms, the commercial grade of glycerine, meeting the standards of purity set forth by the United States Pharmacopeia, contains a minimum of 96% glycerol.


A. K. Tosh

The production of fats and oils as a world commodity is a major commercial enterprise. A large percentage is used for food products, and the remainder represents the primary natural source of glycerine. Glycerol derived from this source is known in the industry as "natural" glycerine. The major processes involved in the production of natural glycerine are generally connected with the detergent and fatty acid industries, wherein it is recovered as a co- or by-product. Glycerine is released during a) the saponification of glyceride fats with an alkali, b) during hydrolysis of glyceride fats with water, and c) during the manufacture of higher alcohols.

Soaps made from fats have been used more than 2,000 years, but the origin and chemical structure of glycerol were unknown 200 years ago. The Swedish chemist Sheele accidentally isolated glycerol while heating a mixture of olive oil and lead oxide in 1779. One hundred years later, about the time commercial production of glycerine began, Berthelot suggested synthesis of glycerol from propylene. August marks the tenth anniversary of the opening of the first successful plant for synthesis of glycerol, that owned by the Shell Chemical Corporation at Houston, Tex., where operation began in August, 1948. Four years later the plant supplied a little more than one-fifth of the total amount of glycerine produced in the United States. Today synthetic glycerine plants supply more than one-third of market requirements. At least two methods of synthesis are being employed, both well covered by patents.

The original method involves obtaining propylene by distillation of an oil refinery propane-propylene fraction. The propylene is dried and heated, as required to maintain the desired temperature, and reacted with electrolytic chlorine by direct vapor-phase chlorination to yield allyl chloride. The allyl chloride is processed in one of two ways depending on the by-products desired: a) hydrolyzed to allyl alcohol, which in turn is treated with chlorine and water, then hydrolyzed to glycerol; b) treated with hypochlorous acid to give glycerol dichlorohydrins, which are in turn hydrolyzed to glycerol. A more recent commercial method consists of vapor-phase catalytic oxidation of propylene to produce acrolein. The acrolein is then reacted with hydrogen peroxide to form glyceraldehyde, which is hydrogenated to produce glycerine.

Purification of the hydrolyzed solutions of glycerol from any of these procedures consists of concentration, solvent extraction to remove color bodies and other impurities, refining by distillation to yield a purity of about 99.5% glycerol, and bleaching to meet rigid color specifications.

Since discussion is limited to the detergent industry, this paper will be confined primarily to glycerine as a product derived from fats and oils. Neutral beef fats yield up to 10.7% glycerol while predominantly lauric acid type of oils, such as coconut oils, yield up to 13.5% glycerol because of the variation in the length of the aliphatic chain of the fatty acid radicals involved. Approximately 88 to 92% of this glycerol is recovered in commercial operations.

Where the fats are saponified with alkali as in the kettle process for making soap, the glycerine is separated from the resulting soap by virtue of the insolubility of soap in sodium chloride solutions. Usually a concentration of 10 to 15% sodium chloride is sufficient to render the soap insoluble. The soap is lighter in specific gravity than the salt solution and rises to the top while the glycerine remains soluble in the lower layer or salt solution. The latter, known as ‘‘spent lye’’, is withdrawn for recovery of its glycerine content. Where countercurrent soap-boiling is used, the glycerol content of the spent lye ranges from 10 to 15%.

In fat-splitting, where fats are hydrolyzed with water alone, no salt is necessary for separation since the fatty acids are insoluble and rise to the top of the splitting column. The glycerine-bearing solution from such procedures is known as sweetwater and, depending on the fats used and the water-to-fat ratio, may contain 10 to 18% glycerol. Other splitting methods, such as the Twitchell Process and high pressure autoclaving, yield similar dilute glycerine solutions.

In the sodium reduction process for making the fatty alcohols used as intermediates for certain detergents, an aqueous solution of glycerine and caustic soda is separated by settling from the fatty alcohol and solvent toluene. The aqueous solution may be used for its caustic value in saponification, for instance, and the glycerol may then be recovered.

Generally, from any source, the unit processes involved in recovery are purification of the glycerine-bearing solutions (commonly called ‘‘lye treatment), evaporation, distillation, and bleaching.

Purification of Glycerine Solutions

Regardless of the grades of fats and oils or the method used in processing them, the quality of finished glycerine is greatly affected by the chemical control and techniques involved in recovery and purification. Of prime importance is the maximum removal of organic impurities, from the dilute glycerine-bearing solution, by chemical treatment and filtration prior to concentration.

Spent lye from direct saponification of fats, a most important source, normally consists of an aqueous solution containing 10 to 15% glycerol, 10 to 20% salt, 0.25% soluble soaps, about 0.25% unused alkali as Na_2O, both as free caustic and as sodium carbonate; other organic impurities—variable according to the quality of the fats used—probably 0.10 to 0.20%, consisting of resinous and nitrogenous compounds, color bodies, hydrocarbons, fermentation products, and some small amount of sediment.

The purification of spent soap lye involves four basic steps: a) separation of entrained and as much of the dissolved soap as possible, b) neutralization of the unused alkali, c) precipitation, coagulation, and removal of the remaining soluble soaps and other organic impurities, and d) precipitation and removal of the excess coagulationg chemical.

The first step is to accumulate the spent soap lye in a storage tank for a holding period of at least three to four hours to allow the lyes to cool, assuming that they have been pumped directly from a soap kettle. A portion of the dissolved soap will become insoluble and rise to the surface together with entrained soap and possibly unsaponified fat. It is customary to provide two tanks for alternate use, one to receive fresh spent lye and the other to permit the contents to settle undisturbed. Soap reclaimed from these tanks is returned to the soap kettles at frequent intervals. The second and third steps, neutralization of the unused alkali and coagulation of the impurities, constitute what is known as First Treatment. The fourth step, precipitation and removal of coagulant, is known as Second Treatment. These steps are normally accomplished batchwise.

The alkalies are neutralized with either sulfuric or hydrochloric acid, and the soaps and organic impurities are precipitated usually with aluminum sulfate. Soaps are rendered insoluble by conversion from the soluble sodium salt to the highly insoluble aluminum salt. The aluminum salt also coagulates nitrogenous impurities to form insoluble agglomerates. Other metallic chlorides or sulfates may be used in place of aluminum sulfate as dictated by economic factors.

The choice between hydrochloric or sulfuric acid and between the metallic chloride or sulfate depends not only on the cost of chemicals but also upon other operational factors. Since salt is recovered during evaporation for re-use in the soap kettles, it is important to avoid formation of excessive sodium sulfate during lye treatment. Sodium sulfate has less ‘‘graining power’’ than sodium chloride, tends to give difficulty during evaporation, and is harder to wash free of glycerine. The sulfate content of recovered salt should be maintained at 10% or less and seldom over 15%; otherwise a discard of the salt itself is required. On the other hand, a periodic discard of salt to control sulfate content may be more economical than using hydrochloric acid and aluminum chloride for treatment purpose.

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In starting First Treatment, a sample of the spent lye charge is withdrawn and analyzed for the percentage of unused alkali. From this the amount of acid necessary for neutralization is calculated and added to the charge under constant agitation. The amount of precipitant, aluminum sulfate for example, is usually determined by experience and varies depending on the quality of the lye being treated. This is added to the bath, and after sufficient agitation a sample is withdrawn and filtered. The filtrate should be clear and nearly colorless and have a pH of about 4.5 to 5.0. A portion is tested by adding a few drops of 10% aluminum sulfate solution. If, on heating the test sample to near boiling, no further precipitate is observed, enough aluminum sulfate has been added. A good detailed description of the chemical control in lye treatment has been described by Govan (1). When the batch meets the above tests, it is filtered. A temperature of 180°F. is maintained during treatment to promote good coagulation and assist filtration.

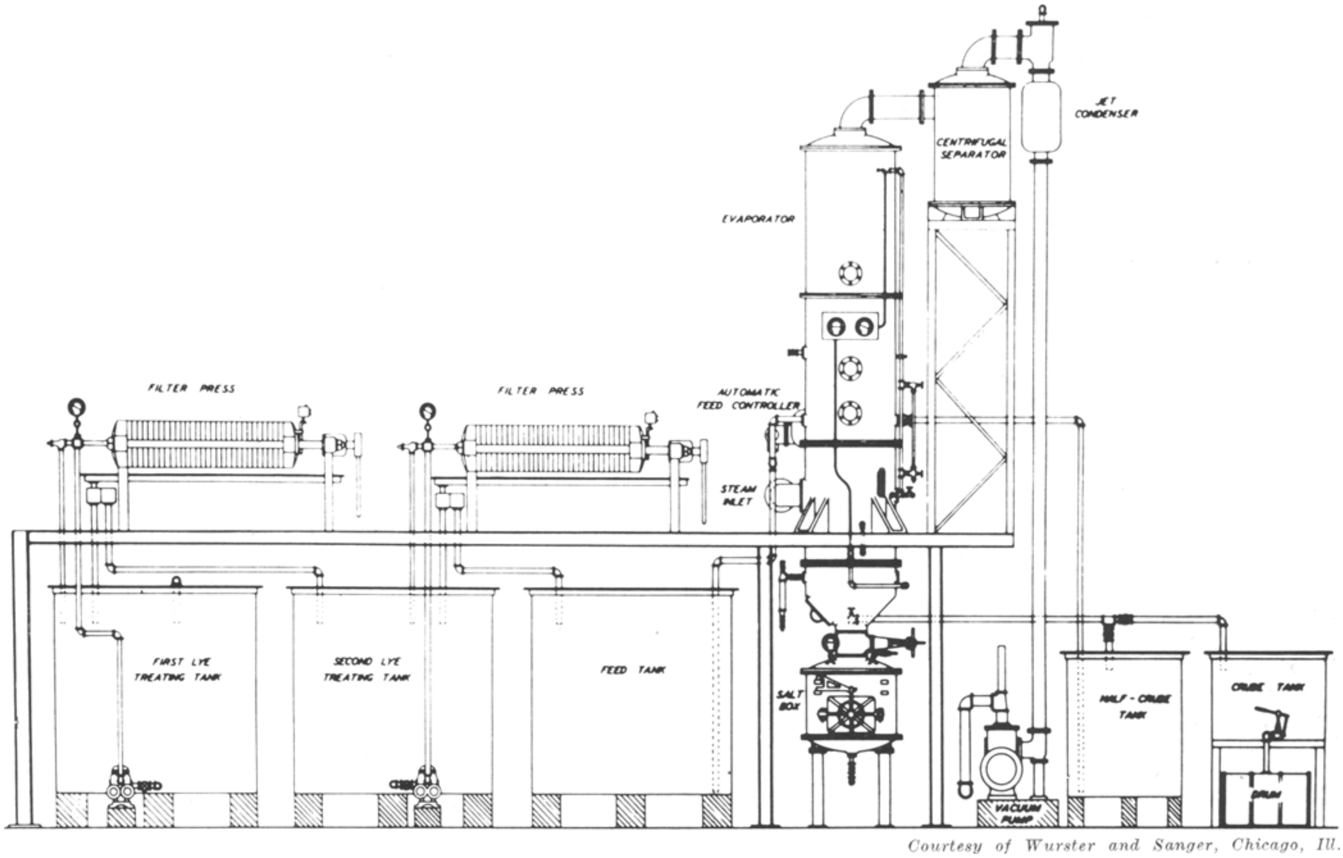
The Second Treatment consists of the removal of excess aluminum sulfate by adding caustic soda gradually to the filtered lye from First Treatment until a sample tested with phenolphthalein turns very slightly pink, or until a pH of 7.5 to 8.5 is established. The precipitated aluminum hydrate so formed is removed usually by filtration. The lye is then ready for evaporation.

The lye treating plant shown in Figure 1 is a rather simple one. The principal equipment for double treatment consists of three wood or steel tanks, two of which are fitted with coils for heating and air agitation; two filter press pumps, and two filter presses of either the plate and frame or recessed plate type. A continuous rotary vacuum filter could also be used. Choice of equipment and materials of construction is based on consideration of the corrosion factors involved. Hot salt solution, either acid or alkaline, presents many problems in corrosion. Steel tanks are often lined with acid or alkali-resistant cement, depending on which treatment is to be made.

The residual cake in the filter presses is washed with water to remove as much glycerine as possible, and the presses are blown with compressed air. Washings are returned to the treatment tank, and the cake is discarded. It is possible to treat sweetwater originating from splitting high-grade fats in a simpler manner, such as addition of a small amount of lime, $Ca(OH)_2$, to precipitate fatty acids, followed by filtration. Sweetwater from splitting low-grade fats is often treated in the same manner as spent soap lye.

Evaporation

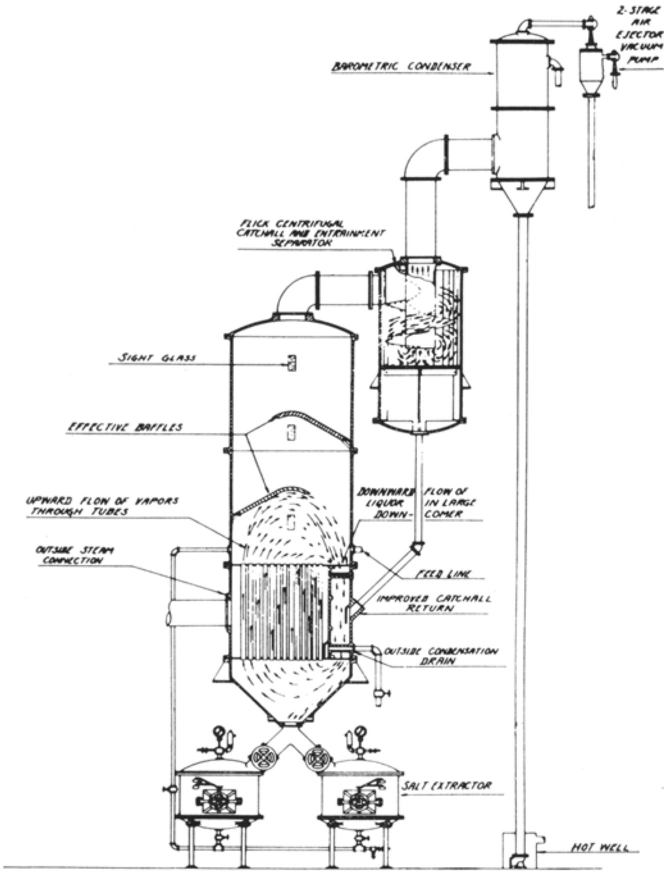
Following purification, the dilute glycerol solutions are concentrated to crude glycerine by evaporation. This is usually carried out in conventional evaporators under reduced pressure with steam as the heating medium. In large plants where exhaust or low-pressure steam is available from the power plant or other operations, single-effect evaporators are normally used. Double-effect evaporators provide economy where live or high pressure steam must be used since twice as much water is evaporated for the same amount of steam. In a double-effect system two evaporators are used in series so that the steam vapors from the evaporated water in the first effect are used as the source of heat for the second effect.



Courtesy of Wurster and Sanger, Chicago, Ill.

Fig. 1. Soap lye treatment plant.

Glycerol solutions may be divided into two types: a) spent soap lye which precipitates salt crystals on concentration, requiring a salt-box type of evaporator; b) sweetwaters which contain only a small amount of sludge and therefore do not require this salting-out feature. Figure 2 illustrates a single-effect evaporator.



Courtesy of Wurster and Sanger, Chicago, Ill.

FIG. 2. Single effect evaporator.

The standard vertical tube evaporator is designed for salting-out solutions and is the one most commonly used for spent soap lye. The evaporator consists of a vertical, cylindrical shell with cone bottom, the lower part of which contains the heating element known as the calandria. This is a vertical bundle of tubes 1½ to 3 in. in diameter by 4 ft. high connected to the source of heating steam, which flows around the outsides of the tubes. The liquor being evaporated circulates upward through the inside of the tubes and downward through an annular space between the evaporator shell and the calandria, known as the "downcomer," setting up a natural circulation.

Above the calandria is a large space provided to permit droplets of liquor in the vapors to fall back into the liquid. From the evaporator the vapors pass through a centrifugal entrainment separator where the vapors are given a centrifugal motion, thus throwing entrained liquid against the walls to drain back to the evaporator. The vapors then pass to a barometric condenser, where the steam is condensed. Noncondensable gas passes on to the vacuum ejectors. A two-stage ejector is sufficient to maintain the 26-28 in. of vacuum normally used in evaporation. The bottom of the evaporator is connected to the salt box, in which the insoluble salt collects during evaporation in the form of a slurry containing about 40 to 50% solids. By means of a valve the salt box can be isolated from the system and the slurry discharged to a slurry tank for the subsequent separation of salt and mother liquor.

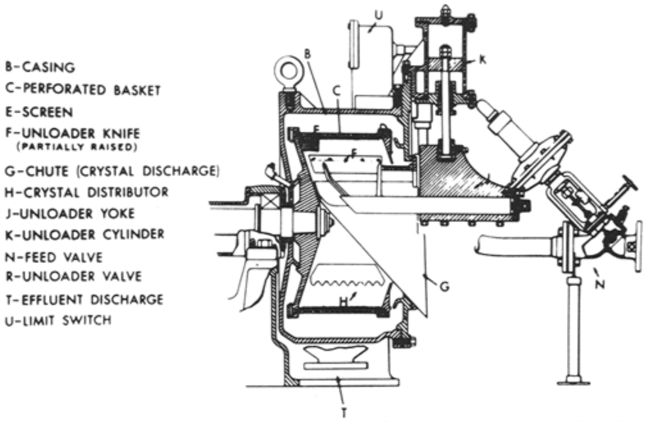
Operation of the evaporator is as follows. Air is evacuated, and the treated soap lye is fed until the calandria is just covered. Steam is admitted to effect boiling, and condensing water is regulated to maintain a vacuum of 26 to 27 in., using a differential temperature in the barometric leg of 5 to 10°F. below the temperature of the vapors being condensed. The end of the feed cycle is established by the temperature of the liquid in the evaporator in relation to the vacuum. The glycerol concentration will be between 80 and 85% when the liquor temperature is 180°F. at 28 in. vacuum. Steam is then shut off, and the vacuum is broken by admitting air to the system. Following a short settling period to allow additional salt to settle, the liquor is decanted to the crude glycerine storage tank. The finished crude will contain 80 to 85% glycerol, 6 to 7% water, 7% dissolved salt, and 1 to 3% impurities not removed in treatment. Although it is possible to evaporate treated lye directly to crude, in large plants evaporation is usually accomplished in two stages by using several evaporators to evaporate to a half crude of 50 to 60% glycerol concentration, accumulating it, and finishing it in one evaporator. Evaporation is stopped at 80 to 85% concentration to prevent abnormal losses of glycerine by vaporization.

Salt Recovery

The salt slurry is separated into relatively dry salt and mother liquor in several ways. An old method, still in use, consists of discharging the slurry from the evaporator salt box to an open tank or filter pan fitted with a perforated screen false bottom. The mother liquor is drained through the salt bed through the perforated screen by pump or vacuum and trapped in a tank, leaving the salt to remain on the screen. Several lye washes and a final water rinse remove the last traces of mother liquor. The nearly dried salt is then shoveled out of the tank. This system requires considerable manual labor, and washing of the salt is inefficient. This method has been supplanted in many instances by centrifuges of either the batch type or the continuous type.

Batch centrifuges are much like the modern top-loading automatic clothes washers on the "spin-dry" cycle. As the slurry is fed to the rotating perforated metal basket, the centrifugal force causes the liquor to pass through the screen to be returned to process. As the feed continues, the salt bed builds up as a layer several inches thick. When the basket is considered to be loaded, the feed is shut off, and water is sprayed on the salt to displace the adhering glycerine. The basket is allowed to rotate to dry the salt, then a plow is employed to discharge the dried salt through a center outlet to a storage bin or dissolving tank for subsequent use as a pickle solution. The cycle is then repeated. Although the batch centrifuge is more efficient than the filter pan, an operator is required to be in attendance.

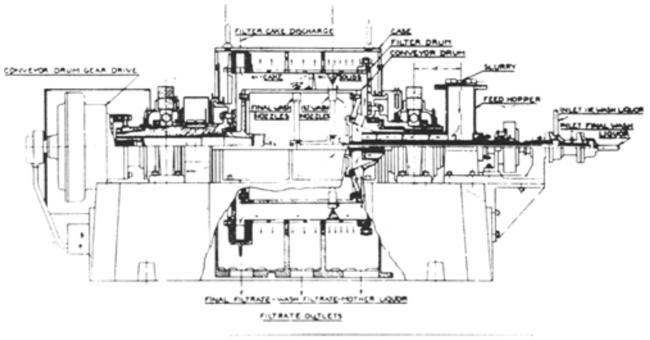
One type of automatic batch centrifuge is the Sharples Super D-Hydrator. This is simply a basket centrifuge, rotated on a horizontal axis, equipped with automatic controls to load, purge, rinse, dry, and unload without stopping. The slurry is admitted through a diaphragm-operated feed valve. A rake distributes the crystals of salt to maintain balance and control cake thickness. The mother liquor escapes through perforations in the basket. After the cake is formed, the feed cuts off and the predetermined rinse cycle is started. Following the rinsing, the cake is dried and finally discharged to storage. Any of the components of the cycle can be changed as desired to effect the best operation for the slurry handled. Figure 3 is a sectional illustration of the Sharples Super D-Hydrator.



Courtesty of the Sharples Corporation, Philadelphia, Pa.

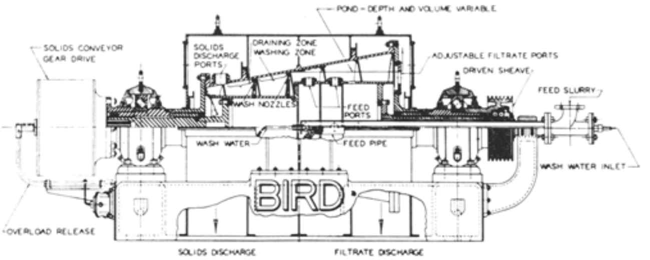
Fig. 3. Section, Sharples Super-D-Hydrator.

The Bird Machine Company makes two types of continuous centrifuges, a screen type which is the most common (Figure 4) and one employing a solid bowl (Figure 5). The screen type consists of a slotted metal drum rotated horizontally. Within is a second drum, called the conveyor drum, which rotates in the same direction but at a slower speed. The slurry fed into one end is spun against the filter drum. The filtrate passes through, and the salt is retained. The plows mounted on the conveyor drum move the cake slowly along the filter toward the discharge end, where it is delivered continuously. Most of the mother liquor is drained from the salt during the first third of traverse over the filter drum. Spray nozzles located on the conveyor drum apply the wash water. The Bird Solid Bowl Centrifuge consists of a truncated cone rotating on an horizontal axis. Slurry is introduced at the large end, and the salt is moved toward the small end by an inner screw conveyor rotating in the same direction as the cone, but at a slower speed. Centrifugal force causes the liquor to drain through the salt bed and along the wall of the cone to be discharged at the larger end. As the salt moves forward, it is carried above the level of the liquid toward the small end of the cone, permitting complete drainage. It finally reaches an area where it is washed with water, using sprays ahead of the conveyor blades. The wash water drains countercurrently, and the washed and finally dried salt is discharged continuously at the small end.



Courtesy of Bird Machine Company, South Walpole, Mass.

Fig. 4. Bird continuous centrifuge (screen type).



Courtesy of Bird Machine Company, South Walpole, Mass.

Fig. 5. Bird Solid Bowl Centrifuge.

The modern automatic centrifuges are highly efficient. Using 0.3 to 0.4 lbs. of water per pound of salt for washing purposes, the finished salt is discharged, containing less than 4% moisture and under 0.5% glycerine. The older methods, such as salt pans, leave considerably more glycerine in the salt besides using much more wash water which must be evaporated. Further the modern centrifuges occupy less floor space and require little manual labor or attention.

Refining of Crude Glycerine: Distillation

Refining of glycerine to meet rigid specifications with regard to purity for food, medicinal, cosmetic, or technical purposes is usually accomplished by distilling to separate the glycerol from the nonvolatile impurities and fractionally condensing the vapors to attain the desired degree of purity. A second relatively new process accomplishes the necessary purification by using ion-exchange resins. The extent to which refining is carried out is largely determined by the use for which the finished product is intended and the specifications under which it is marketed. The vapor pressure of glycerol is 760 mm. at 554°F. Since at temperatures of 400°F. or higher, glycerol will polymerize and decompose to some extent, depending upon the time of exposure, it is not practical to distill at atmospheric pressure. In order to vaporize glycerol at temperatures under 400°F. it is necessary to maintain a greatly reduced pressure in the still or to distill with steam.

Despite the fact that glycerol will vaporize at 338°F. at 10-mm. of absolute pressure, it is normal practice to use a small amount of open steam for two purposes. a) By distilling with steam, the effect is to reduce the partial pressure of the glycerol vapors in the still, assuming the same total pressure is maintained on the still so that the glycerol vaporizes at a lower temperature. As an example, at 45 mm. of pressure, glycerol vaporizes at 400°F. with no steam in the vapor. If steam is injected to reduce the partial pressure of the glycerol vapor to 15 mm. with that of the steam constituting remaining 30 mm., then the glycerol will vaporize at a temperature corresponding

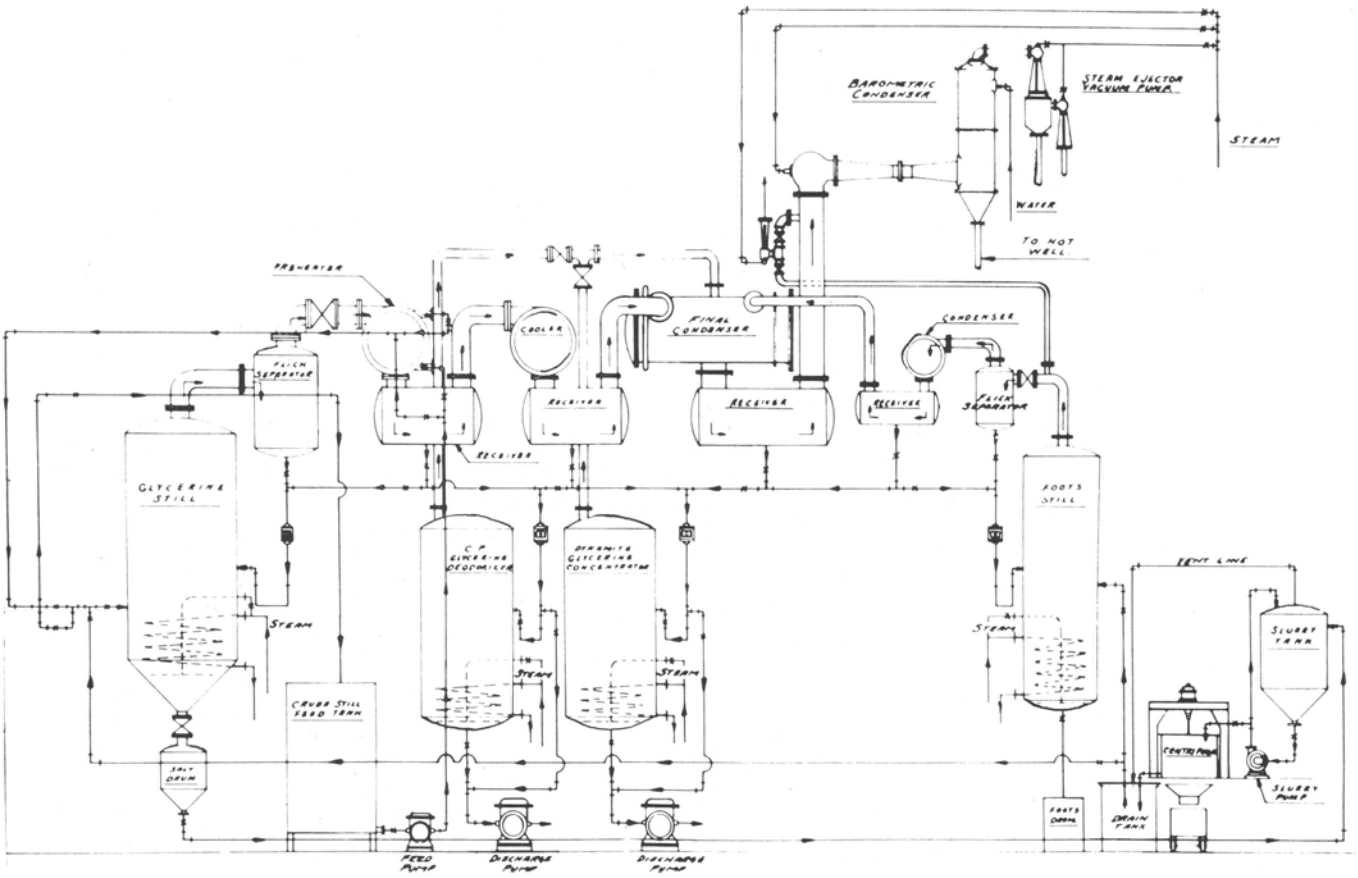


FIG. 6. Wurster and Sanger Continuous Distillation Plant.

to 15 mm. or 347°F.; the use of steam reduces the vaporization temperature from 400°F. to 345°F. with the total pressure remaining at 45 mm. b) Use of open steam serves to agitate the still contents increasing the efficiency of the heating coils. This is important with viscous liquids like glycerine.

Figure 6 illustrates a Wurster and Sanger continuous distillation plant (2). The still is designed to operate at the very low pressure of 6 to 12 mm. in the system. This reduces the amount of open steam required, allows use of relatively low pressure steam, permits distillation at a still temperature of 315 to 320°F., thus resulting in minimum decomposition of glycerine.

After vapors leave the still, they must be condensed. Since they contain water and volatile impurities in addition to glycerol, it is necessary to fractionate the vapors to recover pure glycerol. It is easy to separate the glycerol from water and other volatile impurities by virtue of the wide spread in relative vapor pressures. This is accomplished in the system by passing the vapors through a series of condensers, each operated at a controlled temperature. The one nearest the still is hottest and the others progressively cooler.

In the system shown, steam and water vapors first pass through a centrifugal separator to remove entrained material before entering the condensers. There are three surface condensers, the first also acting as a heat exchanger to preheat crude entering the still. Both the first and second condensers are maintained at a temperature which condenses glycerine but allows the water to pass on as vapor. The third condenser operates at a lower temperature, condensing the remaining small amount of glycerine in the vapors with a little water, but even here the concentration is over 90% glycerol. The glycerine flows into receivers, and the fraction condensing in the first and second condensers, suitable for U.S.P.—C.P. grades, is deodorized by steam passing through it in the receiver, which serves also as a deodorizer. When operating the continuous unit in conjunction with a separate foots still for boiling down final residue, the system can be fed continuously. Removal of settled salt in the primary still and its elimination in the foots by use of a centrifuge results in a high yield of glycerol and low glycerine losses.

Another type of modern glycerine still shown in Figure 7 (3, 4) was developed by the late Martin Ittner of the Colgate-Palmolive Company. Like the Wurster and Sanger still, a low absolute pressure is provided by using a three-stage steam ejector system in conjunction with a barometric condenser. One of the features of this still is the steam economy gained by the exchange of the latent heat of the glycerine vapors with water coming from the heating coils of the still to create the open steam required by the still. This is accomplished in the boiler condenser (H). The condensate from the closed coils (E) of the still goes to the condensate receiver (I), which acts as a flash tank. The pressure drop from 150 to 25 p.s.i.g. results in flashing 10% of the condensate to steam. This steam is relieved (J) to preheat crude in (B) and also the jacket of the feed tank (A). The water from the flash tank flows under pressure to the boiler-condenser (H) where its pressure drops to 5 p.s.i.g. The water is held at a pressure of five pounds by the latent heat of the glycerine vapors and thus generates open steam for the open steam jets (F).

The crude is fed through the preheater to the still, where it is vaporized at about 330°F. The vapors pass through a centrifugal separator, then to the boiler-condenser. Approximately 70% of the total glycerine is condensed at a concentration of about 99.5% glycerol and is used for U.S.P.—C.P. grades. Practically all of the remaining glycerine in the vapors is condensed in the second condenser (M) at a concentration of 99.0 to 99.2% glycerol. This fraction is used for high-gravity grades. The final condenser (O) removes the final 1 to 2% glycerine at about 95% concentration.

Bleaching

Much of the coloring matter remaining in the glycerol solutions after treatment is concentrated in the crude glycerine, which varies in color from a light yellow to dark brown depending on the source. Most of the color bodies are removed during distillation, but some small amount may be carried over with the vapors as entrainment. The removal of off-odors is also important, and these persist in the various fractions in much the same extent as the color bodies.

The activated carbons possess a very high capacity for adsorption of color and odor substances and are used extensively for such service. The amount of carbon needed depends on the quality of the glycerine being bleached, the degree of color removal desired, and the activity of the carbon. Usual dosage ranges from a few tenths of 1% up to about 1%. Higher dosages may be needed where rigid odor specifications are in effect.

The bleaching process is simple, requiring no more than contacting the glycerine with the activated carbon for thirty minutes to one hour at a temperature around 165° to 175°F. preferably in a stainless steel tank, using an efficient agitator. High temperatures should be avoided to prevent developing color.

The mixture is then filtered, using a small amount of diatomaceous earth filter aid if necessary to assist in clarification or to maintain a good flow rate. Adjustment of the concentration with distilled water, when necessary to meet specifications, is normally accomplished just before or following filtration.

The finished glycerine is then pumped to tank cars or tank trucks or poured into drums and cans. To avoid loss of glycerine remaining in the bleach press cake after draining, it is customary to remove the cake and add it to a batch of spent lye prior to First Treatment.

Ion-Exchange Purification (5)

The first commercial unit for purification of glycerine by ion-exchange, designed by the Illinois Water Treatment Company of Rockford, Ill., was built for Lever Brothers Company and placed in operation in

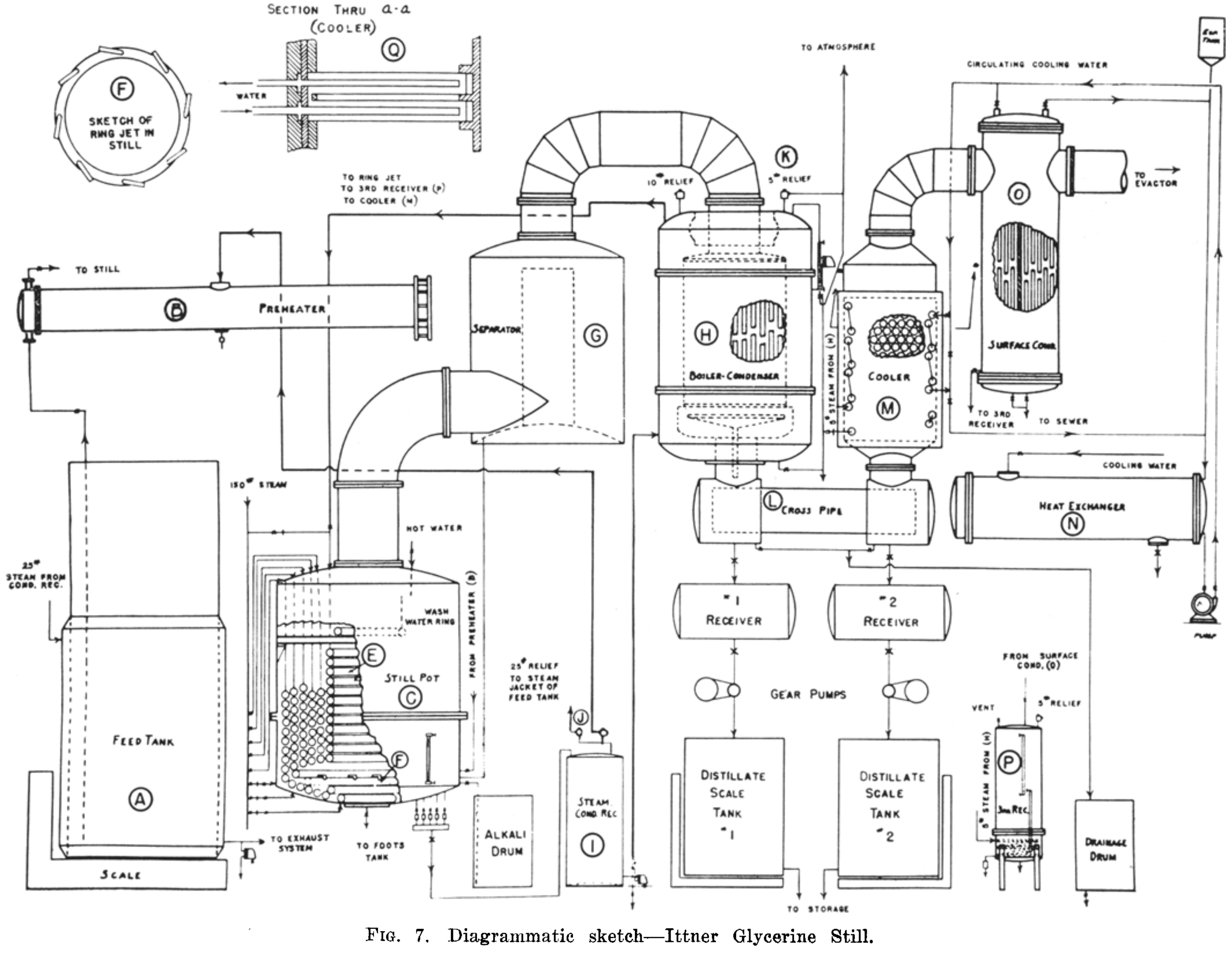


Fig. 7. Diagrammatic sketch—Ittner Glycerine Still.

1951 at their manufacturing plant in Los Angeles, Calif.

Glycerine purified by ion-exchange is equal to and in many cases superior to that obtained by conventional distillation methods. The process is similar to that used for demineralization of water in that ionizable impurities such as sodium chloride, sodium sulfate, mineral ash or other salts, fatty acids or soaps, and color bodies can be removed by cation-anion exchange units in series. Glycerine, being non-ionizable, passes through unchanged and relatively pure so that it needs nothing but concentration by evaporation. Certain impurities such as polyglycerol, glycols, or esters are not removed but fortunately are present only in insignificant amounts.

Sweetwater from splitter operations can be purified directly by this process. Salvage of dilute low-grade glycerine solutions formerly discarded is also very attractive economically since C.P. grade glycerine can be obtained with several passes through ion-exchange equipment, followed by evaporation. On the other hand, spent soap lye with a salt content in the range of 10 to 15% is usually evaporated to an 80% crude to remove most of the salt and make the ion-exchange more economical and practicable. Such crude is then diluted to 25 to 30% glycerol to reduce viscosity for optimum flow rates and also lower the concentration of the remaining salts. In all cases the solutions must be free of fats or turbidity to avoid fouling of the exchange resin beds; otherwise they must be filtered.

The resins used for removal of salt and color are the same types as those used for water purification, but choice of proper resins is important. A cation-exchange resin will remove sodium ions from solutions containing sodium chloride, replacing them with hydrogen to form hydrochloric acid. Passing the same solution through the anion-exchange bed will replace the chlorine ions with hydroxyl ions to form water. Cation-exchange resins frequently used are insoluble condensates of phenol sulfonic acid and formaldehyde or sulfonated polymers of styrene and divinylbenzene. Anion resins, the weak-base type for removing strong acids, are often condensation products of aliphatic amines and phenol with formaldehyde. The strong-base type of resin, for removing weakly ionized organic and inorganic acids, is frequently a quaternerized polymer of styrene and divinylbenzene.

Since a single pass through ion-exchange beds is not 100% efficient, the process is designed to make multiple passes in series. Each succeeding pair of exchangers is smaller in size so that regeneration for all units will be required at the same time. The number of units used depends on the quality of the glycerine solution to be purified and the degree of purity desired. With sweetwater one or two stages plus a "mixed bed" may be used while diluted crude requires three stages plus a "mixed bed" as a final stage. The "mixed bed" removes final, minute traces of impurities and is a well-mixed bed of cation and anion resins. A ratio of one part cation to two parts anion exchanger is normally used.

The process consists of pumping the glycerol solution at 95°F. through the units at a prescribed rate. Since the beds are kept covered with water when not being used, the first portion of the charge is run to a separate tank for use in diluting subsequent batches of crude. When the glycerol content of the effluent is at a proper level, the purified solution is diverted to the product tank. When the charge cycle is completed, water is used again to displace the glycerine solution in the exchangers.

Regeneration of the cation-exchange resin is accomplished by using dilute (12%) sulfuric acid and rinsing with raw water. The anion-exchange resins are regenerated with a dilute solution (5%) of sodium hydroxide and rinsed with treated water. The mixed bed is first separated by backwashing. The lighter anion resins rise to the top, and the cation resins drop to the bottom. Each is regenerated in the same manner as individual beds; caustic solution is passed through a top inlet and acid solution through a bottom inlet. Each solution is drawn off at the interface. After rinsing the resins are mixed by air agitation.

The final operation is to concentrate the purified solution to meet the specifications for a particular grade of glycerine, such as U.S.P. If concentration is done in an evaporator made of stainless steel, no bleaching is required.

Ion-Exclusion (6)

About three years ago a technique developed by the Dow Chemical Company was reported, which uses ion-exchange resins to effect a separation of ionic salts from nonionic glycerine in aqueous solution without actual ion-exchange and without use of chemical regenerants. The process, called ion-exclusion, uses water for elution and depends on a phenomenon known as the Donnan equilibrium effect to obtain separation.

When an ion-exchange resin is placed in an aqueous solution of several solutes such as sodium chloride and glycerine, the high ionic concentration within the fine resin bead causes a difference in the concentrations of the solutes within and outside the resin. The electrolyte is excluded from the interior of the resin bead and the nonelectrolyte, glycerine, is not, thus producing a difference in the distribution of these substances between the resin and solution phases. Thus the two solutes will travel down an ion-exclusion column at different rates and in different order. In the case of sodium chloride and glycerine the ionic solute, sodium chloride, will appear in the effluent prior to the nonionic solute. The ion-exchange resin used for the initial pilot plant work was strongly acidic cation-exchange resin of the sulfonated polystyrene divinylbenzene copolymer type.

The operating conditions to be considered for the ion-exclusion process are: flow rate, particle size of the resin, temperature, volume of feed, cross-linking or percentage of divinylbenzene, and concentration of the ionic and nonionic components. The simplest method of operation consists of filling a column to the desired depth with ion-exchange resin and flooding it with water. A volume of feed solution (diluted crude glycerine, for instance) less than the bulk resin volume, is then distributed over the top of the resin bed. After the feed solution has passed down the column at a constant flow rate and all of the feed has entered the top of the resin bed, flow is continued by elution with water. An aqueous solution of the ionic material comes out of the column first, followed by an aqueous solution of the nonionic material.

A plant using this process has demonstrated that glycerol from soap lye crude can be separated from at least 80% of the dissolved salts. The concentration of glycerol in the effluent is approximately 15%, and losses are in the range of 2 to 4% glycerol. This product from the ion-exclusion process, when further purified by ion-exchange and concentrated, compares favorably with the product from other methods of purification. The technique affords a means for economies in regeneration costs connected with ion-exchange purification in that the bulk of the ionic material can be removed by this method and the remainder by conventional ion exchange.

Acknowledgment

We wish to acknowledge with thanks the assistance given by W. A. Peterson, who provided data for portions of the text and all but one of the illustrations used for this presentation.

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Glycerine: Its Economics and Applications

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THIS HISTORY OF GLYCERINE is quite unlike that of recent developed industrial chemicals, with their planned, rational progress, moving step-by-step from laboratory to pilot plant to market development to full commercial sale. For 150 years glycerine has responded to insight and accident, developing markets along unexpected lines, more influenced by outside forces and discoveries than by glycerine technology itself.

Its discovery first came because lead plasters, formulated with litharge and olive oil, were popular pharmaceutical necessities about the time of the American Revolution. The great Swedish pharmacist, Carl Wilhelm Scheele, brought a true scientific spirit to his routine chores in their manufacture. He became interested in the sweet-tasting liquid resulting from the action of lead oxide on the olive oil, a component of the cooling water as the plaster was stretched and kneaded. Scheele described this substance in his notes in 1779, indicating how its properties differed from sugar syrup. Four years later, in a communication to the Royal Academy of Sweden, he reported that all fats contain this ''natural sweet principle.''

A full explanation of the relationship between fats, fatty acids, and glycerine was developed later by the French chemist, Michel Chevruel, between 1813 and 1820 and was published in a work still regarded as a chemical classic. Not only did he name glycerine, but he patented the first process intended for its production. This was our old friend, saponification, followed by hydrolyzing the soap with sulfuric acid and recovering glycerol from the water.

In the United States, too, glycerine has had a similar pharmaceutical origin. About 1840 a Philadelphia druggist, Robert Shoemaker, began following Scheele's lead plaster procedure. He found a market for small quantities of glycerine at a price of $4 a pound. From 1840 to 1850 production in the United States remained a few hundred pounds or so a year, all used as a pharmaceutical specialty. Meanwhile glycerine's useful physical properties as a solvent and for viscosity and moisture control were becoming better known.

In the 30 years from 1850 to 1880 the first great period of change took place. In this period the quantities consumed industrially came to be reckoned in millions of pounds per year. At the same time the price of glycerine went from several dollars a pound to about 18¢.

The initial recovery of glycerine from fats came, not in soapmaking, but from the production of stearine candles. A soapmaking treatise of 1869 makes no mention of glycerine recovery. At that time however large amounts of tallow were being saponified with lime, and the resulting calcium soap was acidulated with sulphuric acid to yield fatty acids. Recovery of glycerine from the waste water followed.

The fact is that the big boost to glycerine recovery came from outside these industries: it was the discovery of nitroglycerine and its practical employment in the form of dynamite about 1866. Once the demand for glycerine from this source took on major proportions, fat-splitting methods and soap-making methods were revamped to maximize glycerine recovery and steam distillation was quickly improved. By 1880 the enormous waste of glycerine in the manufacture of soap was recognized, and patents for various types of salting-out evaporators were being issued. Within the next 10 years soap lye crude became the dominant glycerine source. At the same time various methods of hydrolysis before saponification—autoclave-splitting, Twitchell-splitting, and the high-pressure, continuous splitter, followed the course set by the candle-maker. By 1900 world production of glycerine was about 100 million pounds, about one-third of which was made in the United States. With the exception of some textile-softening use, almost all went into dynamite.

Recently The New Yorker ran a series of articles on the life and times of Alfred Nobel that gave a lively concept of the early development of dynamite and blasting gelatin from the 1860's onward. There were dozens of examples, even after the product became commercial, of death and destruction arising from unstable materials and from the processing and handling of nitroglycerine. Today's rocket failures and school-boy experimentation are minor by comparison. But again, by about 1900, the dangers had been brought well under control.

Some fascinating economic interrelationships between glycerine and world history came about *via* dynamite. The tremendous surge in mining after