

# Glycerin Production and Refining

W. A. PETERSON, Colgate-Palmolive-Peet Company, Jersey City, New Jersey

IN this discussion we will describe the unit processes involved in the recovery of glycerin as a co-product of the soap and fatty acid industries. It should be mentioned that while glycerin is being produced also by a synthetic process from propylene, since the discussion is limited to the soap and synthetic detergent industry, this paper will be confined to glycerin as a product derived from natural glyceride fats and oils.

Glycerin is released during the saponification of glyceride fats with an alkali or during the hydrolysis of glyceride fats with water. Since the fats used in soapmaking are triglycerides, one molecule of glycerin is formed for each three molecules of soap or fatty acid. Since the glyceryl radical has a constant molecular weight while the fatty acid radical varies in molecular weight according to the length of the aliphatic chain, the amount of available glycerin varies according to the molecular weight of the fatty acids existing in the fat. For example, neutral beef or hog fats yield 10.7% glycerin while the lauric acid type oils, such as coconut, babassu, and palm kernel, yield 13.5-13.9%. In commercial practice 88-92% of this glycerin is recoverable.

The unit processes involved are:

- a) Purification of the glycerin bearing solutions (commonly called "lye treatment")
- b) Evaporation
- c) Distillation
- d) Bleaching

## Purification (Lye Treatment)

Where the fats are saponified with alkali as in the kettle process, the glycerin is separated from the resulting soap by virtue of the insolubility of soap in sodium chloride solutions. Usually a concentration of 10-15% sodium chloride is sufficient to render the soap insoluble. The soap is lighter in specific gravity than the solution and rises to the top while the glycerin remains soluble in the lower layer, which is known as "spent lye" and is withdrawn for the recovery of its glycerin.

Where countercurrent soap-boiling is used, the glycerin content of the spent lye will usually be 10-12%, sometimes up to 15%.

Where the fats are hydrolyzed with water alone, as in fat splitting, no salt is necessary for the separation since the fatty acids are insoluble and rise to the top of the splitting column. The glycerin-bearing solution in this case is known as "sweet water" and, depending upon the fats used and the water to fat ratio used in splitting, may contain up to 15-20% glycerin.

In the case of spent soap lye the solution will contain impurities such as unused caustic soda, sodium carbonate, soaps of low molecular weight fatty acids which are slightly soluble in salt solutions, mechanically entrained soap, color bodies, and nitrogenous impurities. In general, spent soap lye contains more impurities than sweet water since the soaps are not as completely insoluble as are the fatty acids, and there will always be some residual alkali present from kettle saponification. Further, in fat splitting more of the non-glyceride impurities remain in the fatty acid layer.

It is necessary to remove these impurities as far as possible prior to evaporation and distillation, otherwise it would be impossible to conduct the subsequent operations efficiently and a very impure product would result. The treatment of spent soap lye involves two basic factors: a) neutralization of the unused alkali (sodium hydroxide and sodium carbonate chiefly); b) precipitation and coagulation of the soaps and other organic impurities.

The alkalis are neutralized with either sulphuric or hydrochloric acid, and the soaps and organic impurities are precipitated by an aluminum or iron salt such as the sulphate or chloride. Soaps are rendered insoluble by conversion from the soluble sodium salt to the highly insoluble metallic salt. The aluminum and iron salts also coagulate nitrogenous impurities to form insoluble agglomerates.

The choice between hydrochloric or sulphuric acid and between the metallic chloride or sulphate depends not solely on the cost of chemicals but also upon other operating factors. Since the salt is to be recovered during evaporation for re-use in the soap kettles, it is important to avoid the formation of too much sodium sulphate during lye treatment. Sodium sulphate has far less "graining power" than sodium chloride. Further, sodium sulphate is harder to wash free of adhering glycerin. In practice it is desirable to hold the sulphate content of the recovered salt to 10% or less, and seldom over 15%; otherwise an eventual discard of the salt itself would be necessary.

The extent of the impurities is approximately:

Soluble soaps—0.25%  
Unused alkali—0.20% as  $\text{Na}_2\text{O}$   
Other organic impurities—variable according to quality of fats used, probably 0.10-0.20%

The first step is to accumulate the spent soap lyes in a storage tank for a holding period of at least three to four hours to allow entrained soap to rise. In large plants it is customary to provide two tanks for alternate use, one being used to receive new soap lye while the other is resting undisturbed. From the latter the batches for treatment are withdrawn. Soap reclaimed in these tanks is eventually returned to the soap kettles. The treatment is usually done batch-wise in any convenient size, from perhaps 50,000 pounds in a smaller plant to 300,000 pounds or more in a large plant. A sample is analyzed for the percentage of unused alkali, and from this the amount of acid necessary to neutralize it is calculated and added to the charge under constant agitation. The amount of precipitant, aluminum sulphate for example, is usually arrived at by experience and varies according to the quality of lye being treated. This is added to the batch and after sufficient agitation a sample is tested.

Several variations in test procedure are used. The one described here is a simple one that has proved adequate. A sample is filtered, and a portion tested by adding to it a few drops of 10% aluminum sulphate solution. If upon heating to near boiling no further precipitate is observed, enough aluminum sulphate has been added. A confirming test is used to prevent

wastage of aluminum sulphate (in the event that too much was added) by determining the acidity of a filtered sample in terms of sulphuric acid, which at this point should be between 0.08-0.12%. In some plants the pH is used as a control and at this point should be about 4.5. A good detailed description of the chemical control in lye treatment has been described by Govan (1).

When the tests meet specifications, the batch is filtered. The temperature maintained during treatment is usually about 180°F., which assists in the coagulation of the precipitate and assists filtration.

Filtration may be done, using recessed plate or plate and frame filterpresses or a continuous rotary vacuum filter. The cake in the filter is later washed with water to reduce its residual glycerin content to 2-3% since this filter cake is discarded and usually amounts to about 2% of the weight of lye treated.

The foregoing constitutes what is known as the first treatment. The second treatment is merely the removal of the excess aluminum sulphate by adding caustic soda to the filtered lye from the first treatment until a sample is pink to phenolphthalein, or until a pH of 8.5-9.0 is established. The aluminum hydrate so formed is removed by filtration, and the finished lye is ready for evaporation. Figure 1 illustrates the arrangement of a typical plant for the treatment of spent soap lye. The single effect evaporator shown here will be described in greater detail later.

For sweetwaters originating from high grade fats, a simpler treatment is possible, such as the addition of a small amount of lime,  $\text{Ca}(\text{OH})_2$ , to precipitate fatty acids, followed by filtration. When low grade fats are split, the sweetwaters may require practically the same treatment as for spent lye.

## Evaporation

Since the treated soap lyes contain between 10-15% glycerin and about 15% salt, the next operation is to concentrate the solution to a crude glycerin of 80-85% concentration. During the removal of water most of the salt becomes insoluble, which makes it possible to recover this salt for reuse in the soap kettles. The final crude glycerin will contain about 7% of dissolved salt.

Evaporation is done in single or double effect vacuum evaporators. In large plants where exhaust steam is available from the power plant or other operations, single effect evaporators are usually used. Double effect evaporators provide a means of economy where live steam must be used since 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. Therefore approximately twice as much water can be evaporated by a given amount of steam although the evaporator capacity is reduced by about half since two evaporators must be used for the same output as would be obtained from one single effect. Figures 2 and 3 show the arrangement of a single effect and a double effect evaporator.

The evaporator consists of a vertical cylindrical shell, the lower part of which contains the heating element known as the calandria. This is a vertical tube bundle connected to the source of heating steam, which flows around the outside of the tubes. The liquor being evaporated circulates upward through the inside of the tubes and downward through an enlarged open section known as the "down-comer," thus setting up a natural circulation of the liquor.

Above the calandria is a large free space known as the vapor belt, so designed in order to permit droplets

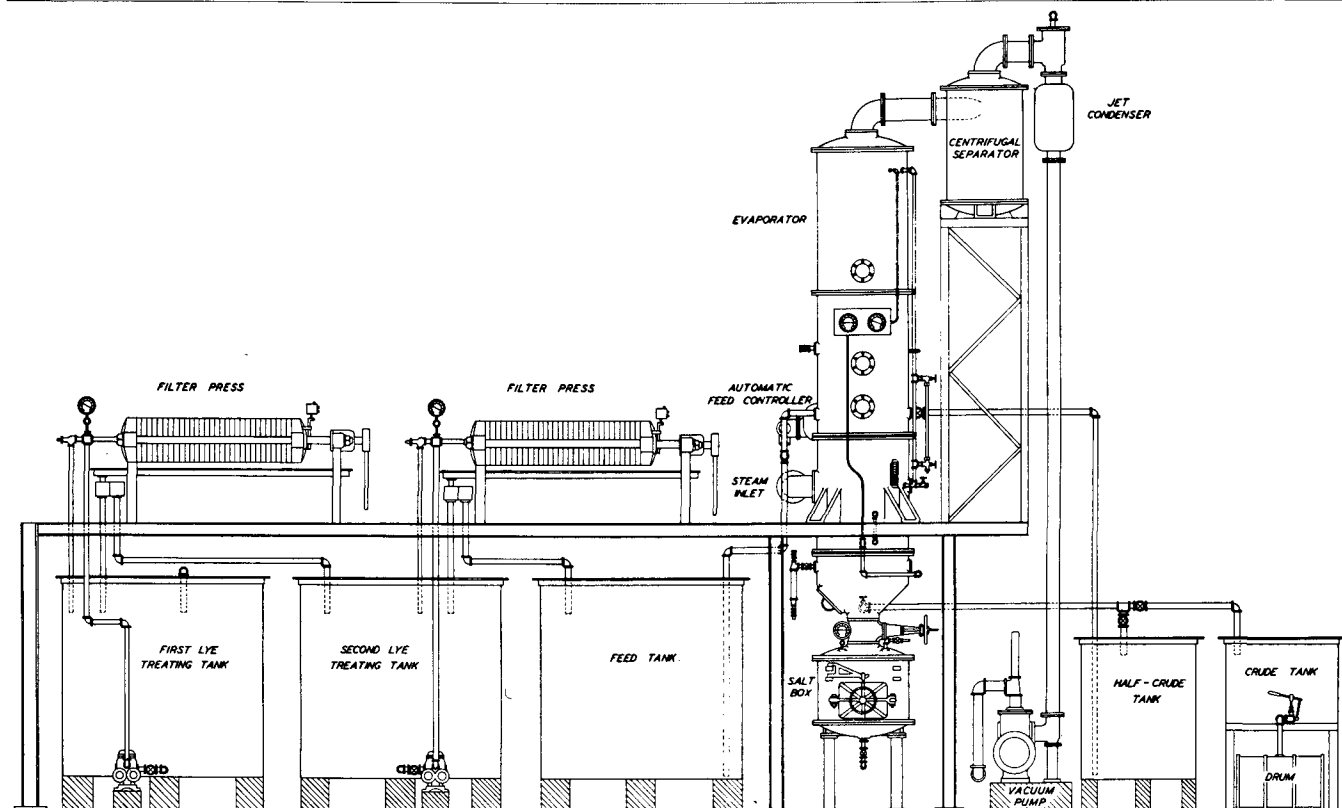


FIG. 1. Soap lye treatment plant.

Courtesy of Wurster & Sanger, Chicago, Ill.

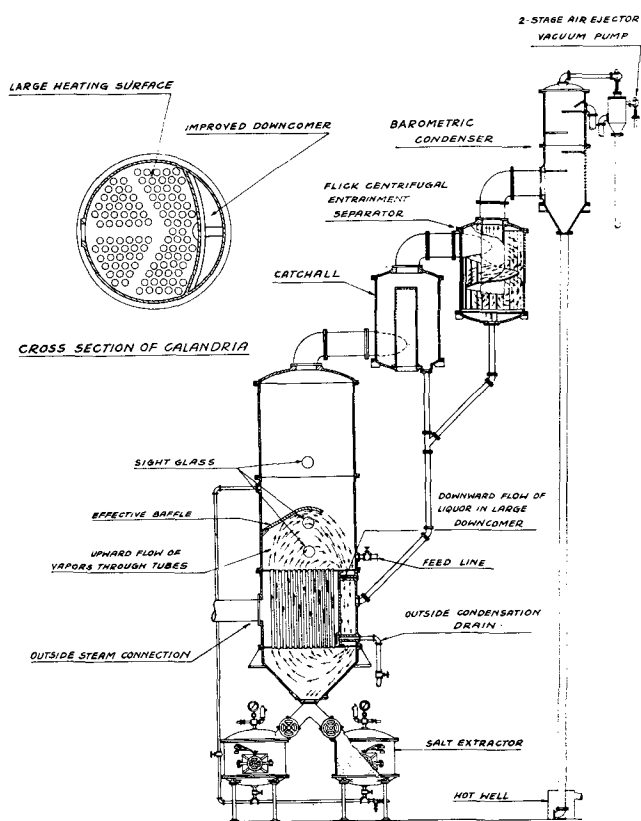


FIG. 2. Single effect evaporator.

Courtesy of Wurster & Sanger, Chicago, Ill.

of liquor in the vapors to fall back into the liquid. The vapor belt is sometimes equipped with baffles to reduce further the possibility of entrainment. After leaving the evaporator, the vapors pass through an entrainment separator, usually of the centrifugal type, wherein the vapors assume a centrifugal motion, thus throwing the fine droplets of liquid to the walls where they coalesce and drain back to the evaporator. The vapors then pass to a barometric condenser where the steam is condensed. Non-condensable gas passes on to the vacuum ejectors. A two-stage ejector is sufficient to maintain the 26-28 inches of vacuum normally used in evaporation.

The bottom of the evaporator is connected to a salt drum (as shown in Figure 3), in which the insoluble salt collects during evaporation in the form of a slurry containing approximately 40 to 50% solids. By means of a connecting valve the salt drum can be isolated from the system and the slurry transferred by air pressure to a slurry tank for the subsequent separation of salt and liquor.

Operation (single effect) is as follows. The air is first evacuated, after which treated soap lye is fed until the calandria is just covered. Steam is turned on gradually to effect boiling, and the condensing water is regulated to maintain a vacuum of 26-27 inches by maintaining a differential temperature in the barometric leg of 5-10°F. below the temperature of the vapors being condensed. The end of the feed cycle is determined by the temperature of the liquid in the evaporator in relation to the vacuum. For example, when the temperature reaches 180°F. at 28 inches vacuum, the glycerin concentration will be between 80-85%.

The feed is then stopped, the condensing water and steam are shut off, and the vacuum is broken by admitting air to the system. The batch is allowed to settle for about a half hour to allow any remaining insoluble salt to settle into the drum, after which the crude is run off to a storage tank. The finished crude will contain between 80-85% glycerol, about 7% salt in solution, 1-3% organic impurities not removed by the lye treatment, and 6-7% of water.

Although it is possible to evaporate as described above direct from treated lye to crude, the more usual operation in a large plant is to evaporate in two stages, using several evaporators to evaporate to a half crude of 50 to 60% glycerin and to accumulate this half crude and finish it in one evaporator.

The reason that concentration is stopped at 80-85% glycerin is that the removal of the last of the water would require higher finishing temperatures, in a range where the vapor pressure of glycerin increases to a point where some would be lost by vaporization.

### Salt Recovery

The salt slurry may be separated into relatively dry salt and mother liquor in a number of ways. One of the older methods is to connect a pair of "salt extractors" directly to the evaporator, as shown in Figure 2. The extractors are cylindrical drums fitted with screens over a rigid perforated plate near the bottom. The drums are used alternately. The salt slurry settles in the drum and, when full, the connecting valve is closed and the bottom valve opened, thus using the vacuum in the evaporator to pull the liquor through the bed of salt and return this liquor to the evaporator. The salt resting on the screen is then steamed to displace most of the liquor, after which the door on the extractor is opened and the salt raked out manually. Another method employed small tanks fitted with a screen above the bottom, and a draw-off connection at the bottom connected to a vacuum pump with a liquid trap in between. By this arrangement the slurry is flowed into the tank, and the salt is held by the screen while the liquid passes through the bed of salt and the screen and is pulled into the trap by the vacuum pump. The bed of salt could then be washed with water to remove adhering glycerin. This arrangement is very similar to a laboratory Gooch filter. This system requires considerable manual labor since the salt has to be shoveled out of the tank, and the process is slow and the washing of the salt inefficient. These methods have largely been superseded by centrifuges of either the batch type or the continuous type.

Since the separation of solids in this case is based upon sedimentation, it is easy to understand the value of a centrifuge. For example, if a centrifuge is designed so that when rotated at 1,000 RPM a force equal to 500 times that of gravity is developed, the result is that a particle weighing one ounce will act as though it weighed 500 ounces in the centrifuge. Thus relatively small particles are made to behave as pebbles, and the separation is speeded up tremendously. Depending upon the size and speed of the centrifuge, forces over 1,000 times that of gravity are possible.

The batch centrifuge consists of a perforated metal basket rotated on a vertical axis, fitted with a metal screen. As the slurry is fed to the rotating basket, the centrifugal force causes the liquid to pass immediately through the screen into a surrounding casing from

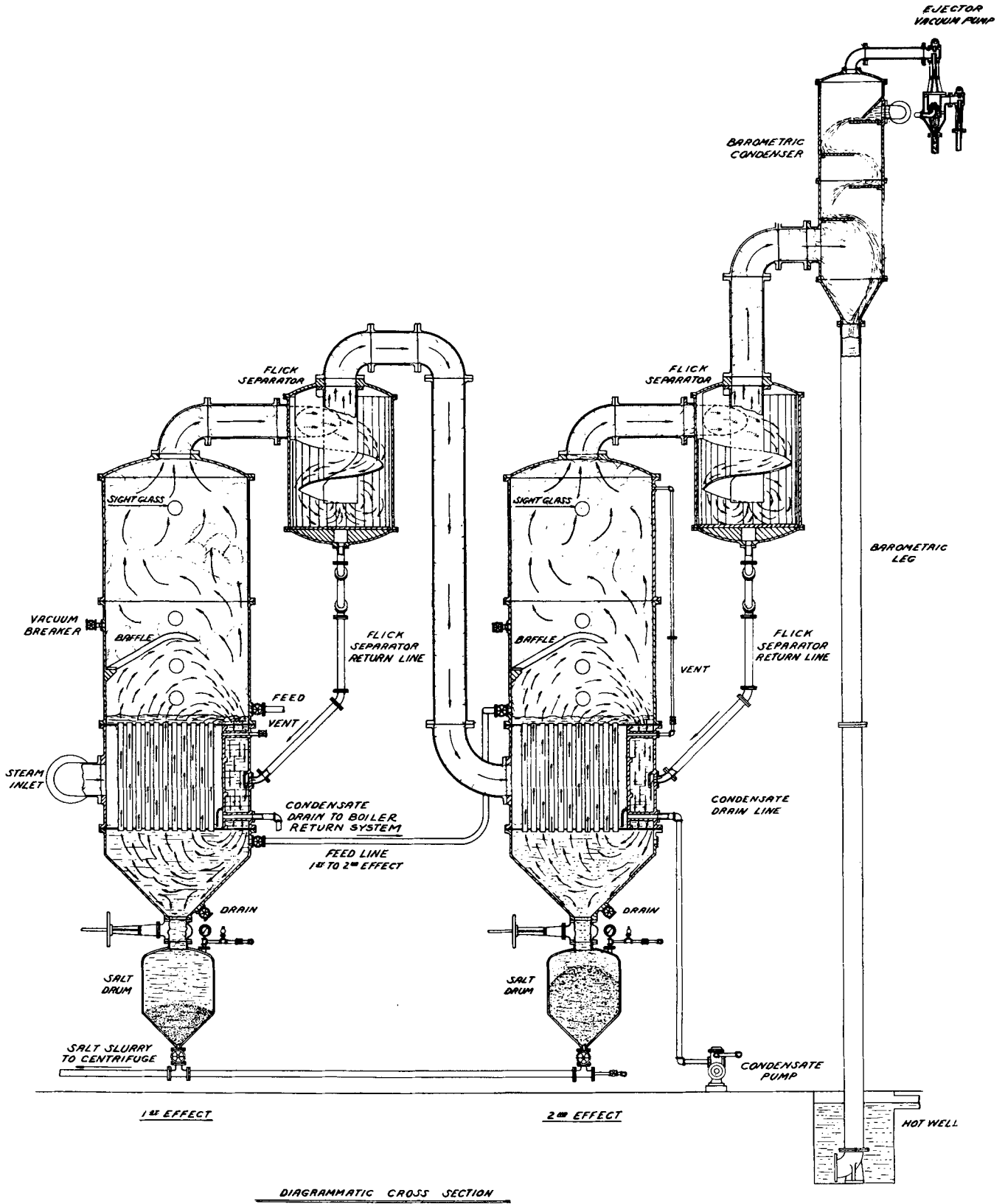
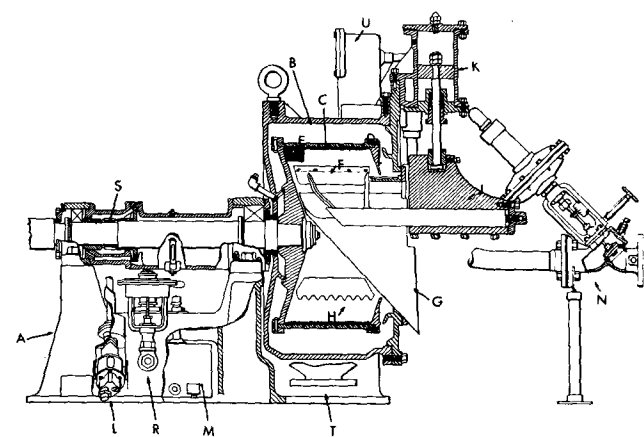


FIG. 3. Double effect evaporator.

Courtesy of Wurster & Sanger, Chicago, Ill.



A-FRAME	G-CHUTE (CRYSTAL DISCHARGE)	N-FEED VALVE
B-CASING	H-CRYSTAL DISTRIBUTOR	P-RINSE VALVE
C-PERFORATED BASKET	J-UNLOADER YOKE	R-UNLOADER VALVE
D-LIP RING	K-UNLOADER CYLINDER	S-PUMP GEAR
E-SCREEN	L-UNLOADER HYDRAULIC PUMP	T-EFFLUENT DISCHARGE
F-UNLOADER KNIFE (PARTIALLY RAISED)	M-HYDRAULIC OIL RESERVOIR	U-LIMIT SWITCH

FIG. 4. Section, Sharples Super-D-Hydrator.

*Courtesy of The Sharples Corp., Philadelphia, Pa.*

which it drains to storage and is returned to the evaporator. As the feed is continued, the bed of salt builds up as a layer several inches thick. After the desired amount of salt has accumulated, the feed is shut off and water is sprayed on the salt to displace adhering glycerin. The basket is then allowed to rotate for a short time to dry the salt, after which it is discharged through a center bottom outlet by means of a plough and the cycle repeated. The batch centrifuge is much more efficient than the older filter pans but still requires the attendance of an operator.

One type of continuous centrifuge is the Sharples Super D-Hydrator, which is really a basket centrifuge rotated on a horizontal axis and equipped with automatic controls to load, purge, wash, dry, and unload

without slowing or stopping the unit and with no manual attention. Any of the components of the cycle can be changed as desired so as to utilize the most effective combination for the particular slurry being handled. The basket rotation is at a high speed (1,800-2,100 RPM), consequently the centrifugal force is magnified to as much as 1,200 times gravity. The whole cycle is complete in about one minute and automatically repeats so that the effect of continuous operation is attained. Figure 4 shows a sectional drawing of the Sharples Super D-Hydrator.

Another type of continuous centrifuge is the Bird Machine Company unit, which is available either in a screen type or in a solid bowl type.

Figure 5 shows a screen type unit which consists of a slotted metal drum rotated on a horizontal axis. Within this is a second drum known as the conveying drum which rotates in the same direction but at a slower speed. The slurry is fed into one end of the unit and is thrown against the slotted drum by centrifugal force, where the salt is retained while the liquor passes through. Ploughs mounted on the inner conveying drum push the salt forward to the discharge end. Spray nozzles are mounted on the conveying drum through which water is sprayed on the salt at the proper section in order to remove adhering glycerin. As the salt moves toward the discharge end, it is automatically purged of mother liquor, washed and dried, and, as it discharges, may be conveyed away to storage.

Figure 6 illustrates the Bird Solid Bowl unit. This has no screen but consists of a truncated cone rotating on a horizontal axis. Slurry is introduced at the large end, and the salt is moved toward the smaller end by means of an inner screw conveyor, rotating in the same direction as the main drum but at a slower speed. Centrifugal force causes the liquor to drain through the bed of salt and along the wall of the cone, draining toward the larger end where it is continuously discharged. As the salt is moved forward, it is carried above the level of the liquid toward the small end of

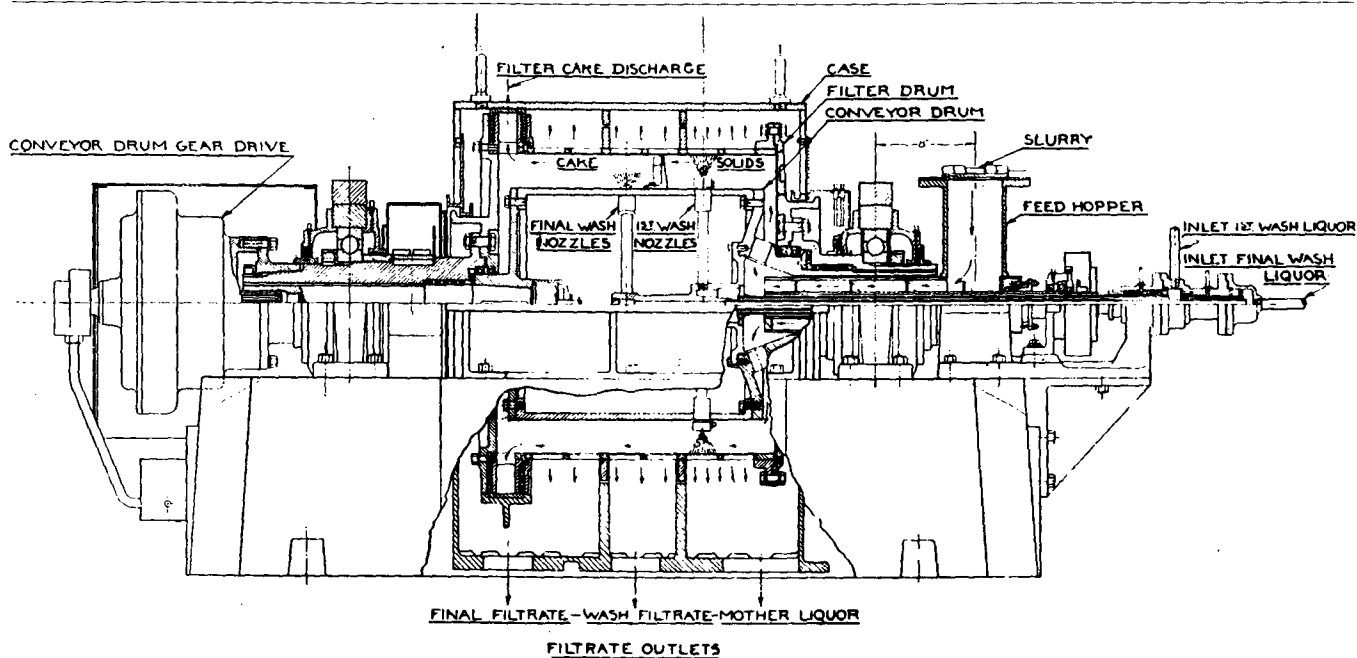


FIG. 5. Bird continuous centrifuge (screen type).

*Courtesy of Bird Machine Company, So. Walpole, Mass.*

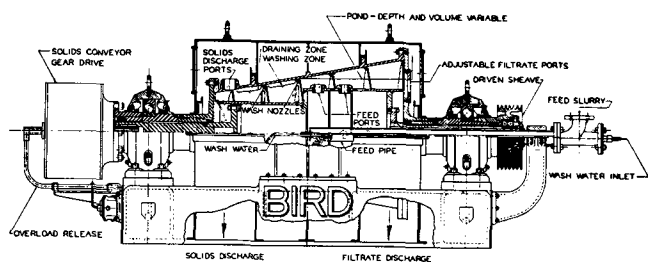


FIG. 6. Bird solid bowl centrifuge.

Courtesy of Bird Machine Company, So. Walpole, Mass.

the cone which permits final drainage of the remaining liquor in the salt, after which it reaches an area where it is washed with water through sprays located in front of the conveyor blades. This wash water also drains down the walls countercurrently to the flow of salt. The washed and dried salt discharges continuously at the small end.

Since in the centrifugal type machines the force of gravity is magnified many times, it is obvious that the separation of salt and liquor is practically instantaneous, and the residual moisture and glycerin content of the salt will be less than in the old vacuum pan system. With a small amount of water, such as 3-4 pounds per pound of salt, the centrifugal machines can deliver salt containing between .2 and .3% glycerin. Somewhat more water will be required in the batch type centrifuge because of its slower speed. The moisture content of the dried salt from a continuous high speed centrifugal machine will be about 3-4%. In the old style vacuum pans it was difficult to wash the glycerin out of the salt below .5-1.0% and even this

had to be accomplished by repeated washings with much larger quantities of water. The importance of recovering this salt with as little glycerin in it as possible lies in the fact that this salt is reused in the soap kettles and it has been estimated that about 25% of whatever glycerin is left in the salt will be lost when the salt is reused. Not only do the modern centrifuges minimize this loss but much less floor space is required for any given tonnage of salt to be recovered, and in the continuous units manual labor is practically unnecessary except for occasional attention.

### Distillation

The crude glycerin is brown in color and contains salt and organic impurities which must be removed to produce the pure glycerin known to commerce. Up until very recently the only process for accomplishing this was distillation. More recently the purification of crude glycerin by ion exchange has been developed and will be discussed later. It will be impossible within the scope of this discussion to describe all of the various designs of distillation units that have been used. Therefore we will confine this discussion to a description of two of the modern units in use; namely, the Wurster and Sanger distillation unit, which has been described by Wurster (2), and the Ittner still (3), which has been described by Peterson (4).

At atmospheric pressure the boiling point of glycerin is 554°F., or stating it differently, 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 exposed to this temperature, it is not possible in practice to distill at atmospheric pressure.

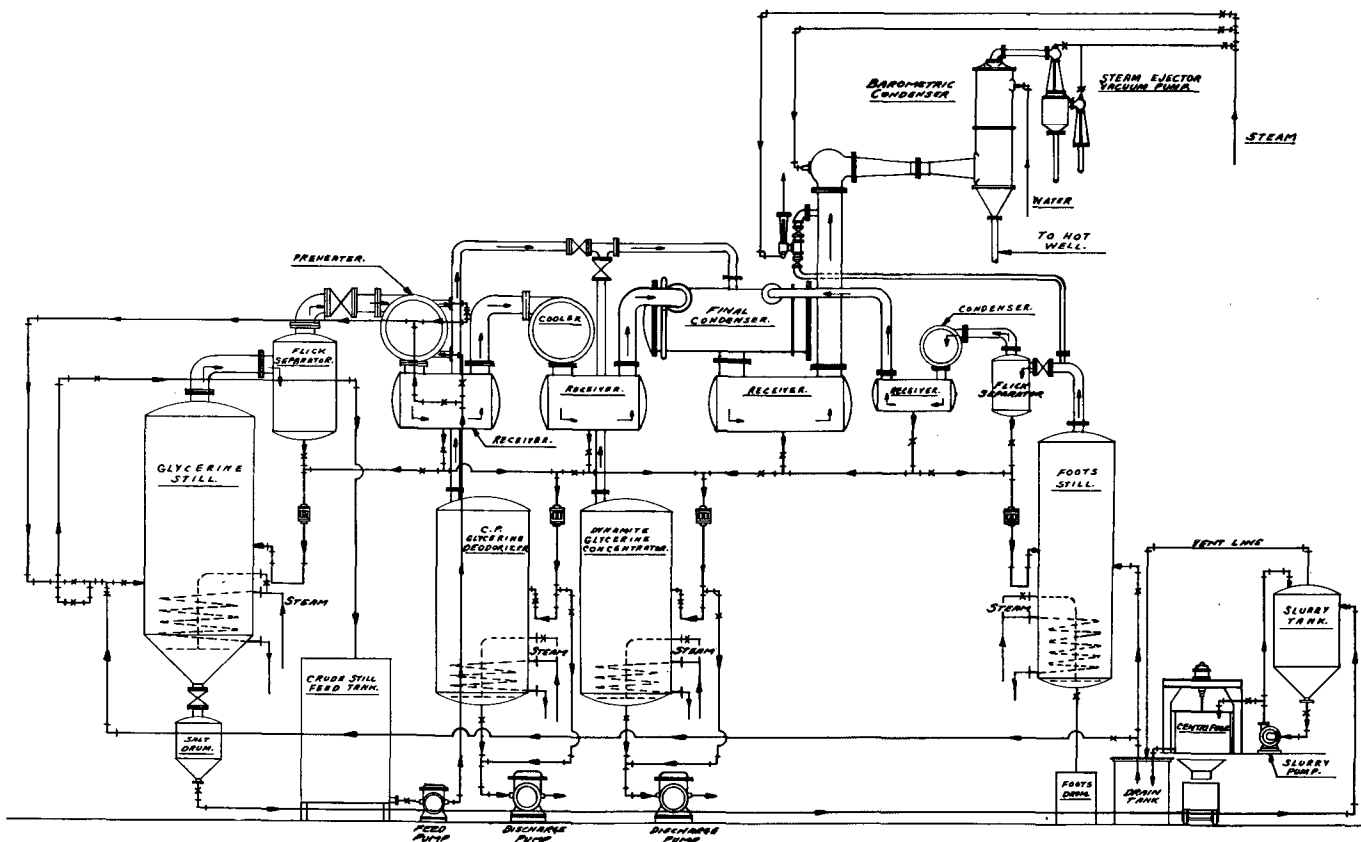


FIG. 7. Wurster &amp; Sanger continuous distillation plant.

It is possible to distill without open steam if the pressure is low enough. For example, glycerol will vaporize at 338°F. at 10 mm. absolute pressure. However it is usually the practice to use a small amount of open steam for two reasons:

a). By reducing the partial pressure of the glycerol vapors, it is possible to distill at even lower temperatures. To use an exaggerated example, at 45 mm. pressure glycerol will vaporize at 400°F. with no steam in the vapor, but if steam is injected so as to reduce the partial pressure of the glycerol vapor to 15 mm., with that of the steam constituting the remaining 30 mm., then the glycerol will vaporize at 347°F., with the total pressure remaining at 45 mm. Under the distillation conditions used in practice the following equation will apply approximately:

$$\frac{\text{Wt. Glyc. Vapor}}{\text{Wt. Water Vapor}} = \frac{\text{Partial Press. Glyc. Vapor}}{\text{Partial Press. Water Vapor}} \times \frac{\text{M. W. Glyc.}}{\text{M. W. Water}}$$

Solving this for the values given, the amount of steam required is 0.39 pounds steam per pound glycerin distilled.

b) The use of open steam serves to agitate the contents of the still, thus increasing the rate of heat transfer from the heating coils. This is important with viscous liquids like glycerin.

Obviously, the lower the total pressure in the still, the less open steam will be required for any desired distillation temperature. Modern stills take advantage of this fact by using three-stage steam ejectors to reduce the pressure to about 10 mm. The resulting reduction in open steam requirement provides for more economical sizing of vapor lines and barometric condensers.

Figure 7 shows the Wurster and Sanger continuous distillation unit. A feature of this still is the low pressure of 6 to 12 millimeters absolute in the system, which greatly reduces the amount of open steam required and allows the use of relatively low pressure for the heating steam (100 P.S.I.G.), which permits distillation at a temperature in the still of 315-320°F., resulting in a minimum decomposition of glycerin. Further, through control of the temperature of the condensers, it is possible to condense all of the glycerin in a highly concentrated form. Another interesting feature is the use of a salt drum underneath the still so that salt accumulating as the glycerol is removed during distillation can be isolated and removed for separation of the solid salt in the slurry, with subsequent distillation of the liquor, resulting in a low residual loss of glycerin in the foots.

Steam and glycerin vapors leaving the still are passed through a centrifugal separator to remove entrainment. The vapors are condensed in a series of three surface condensers, the first of which acts as a heat exchanger to preheat the crude entering the still. Both the first and second condensers are maintained at a temperature that will permit the glycerin to condense but the water to pass on as vapor. The third condenser is operated at a somewhat lower temperature and condenses the remaining small amount of glycerin in the vapor with a little water, but even here the concentration is over 90% glycerin. The glycerin from the condensers flows into receivers and the fraction which condenses in the first and second condensers, which is suitable for U.S.P. grades, is deodorized by steam passing through it in the receiver, which serves also as a deodorizer.

When this type of continuous unit is operated in connection with a separate foots still for boiling down the final residue, the system can be fed continuously. The removal of salt from the liquor by centrifuging results in a much lower loss of glycerin in the final "foots," which must be discarded. With a direct boil-down in a batch still the foots loss will be about 3-4% of the glycerin fed, but with the separation made possible in the Wurster and Sanger still, together with the low distillation temperature, the foots loss can be reduced to about 1%.

In modern stills, such as this, many of the disadvantages of older units have been eliminated. Through controlled condensation temperatures the vapors can be stripped of all of their glycerin in concentrated form. This eliminates several objections to earlier systems. The condensed glycerin requires little or no concentration to bring it up to the commercial concentrations demanded, which are 95% glycerol for the U.S.P. grade and 98.7% glycerol for the Dynamite grade. There is no sweet water to be re-evaporated and redistilled. In some older type units it was common to obtain between 1-2 pounds of sweet water per pound of glycerin distilled, and this contained only 2 or 3% glycerol, thus requiring re-evaporation and redistillation for recovery. Operation under high vacuum reduces steam costs considerably and minimizes decomposition.

Another type of modern still is the Ittner still developed by Dr. Ittner of the Colgate-Palmolive-Peet Company. Figure 8 illustrates the features of this unit. As in the Wurster and Sanger still, a low absolute pressure is employed by using a three-stage ejector together with a barometric condenser. An interesting feature of this still is that considerable steam economy is gained by exchange of the latent heat of the glycerin vapor with water coming from the heating coils of the still to create the open steam required by the still. This is done in the "boiler condenser." The condensate from the closed coils of the still goes to a condensate receiver (I), which acts as a flash tank. The pressure drops from 150 PSIG to 25 PSIG, causing about 10% of the condensate to flash into steam. This steam is relieved from the flash tank (at J) and used in the preheater (B) to heat the crude going to the still. The jacket of the feed tank (A) for the still also receives some of the steam from the flash tank so that, in effect, two preheating stages are obtained. The water from the flash tank then flows under pressure to the boiler condenser (H), where its pressure drops to 5 PSIG. This water is maintained at 5 pounds pressure by the heat from the glycerin vapors, thus recovering this heat and utilizing it to generate the open steam for the open steam jets (F). The crude is fed through the preheater to the still (C), where it is heated to a temperature of 330°F. by the closed steam coils. The glycerin and water vapors leave the still, passing through a centrifugal separator (G) to the first condenser (H) which is called the "boiler condenser." Since this condenser is maintained at a constant pressure of 5 PSIG, its temperature will be 228°F. This permits condensation of approximately 70% of the total glycerin at a concentration of about 99.5% glycerol. All metal surfaces in contact with glycerin up to this point are of stainless steel, and this distillate fraction is used for U.S.P. grade. The uncondensed vapors pass through a cross-

SECTION THRU Q-Q  
(COOLER)

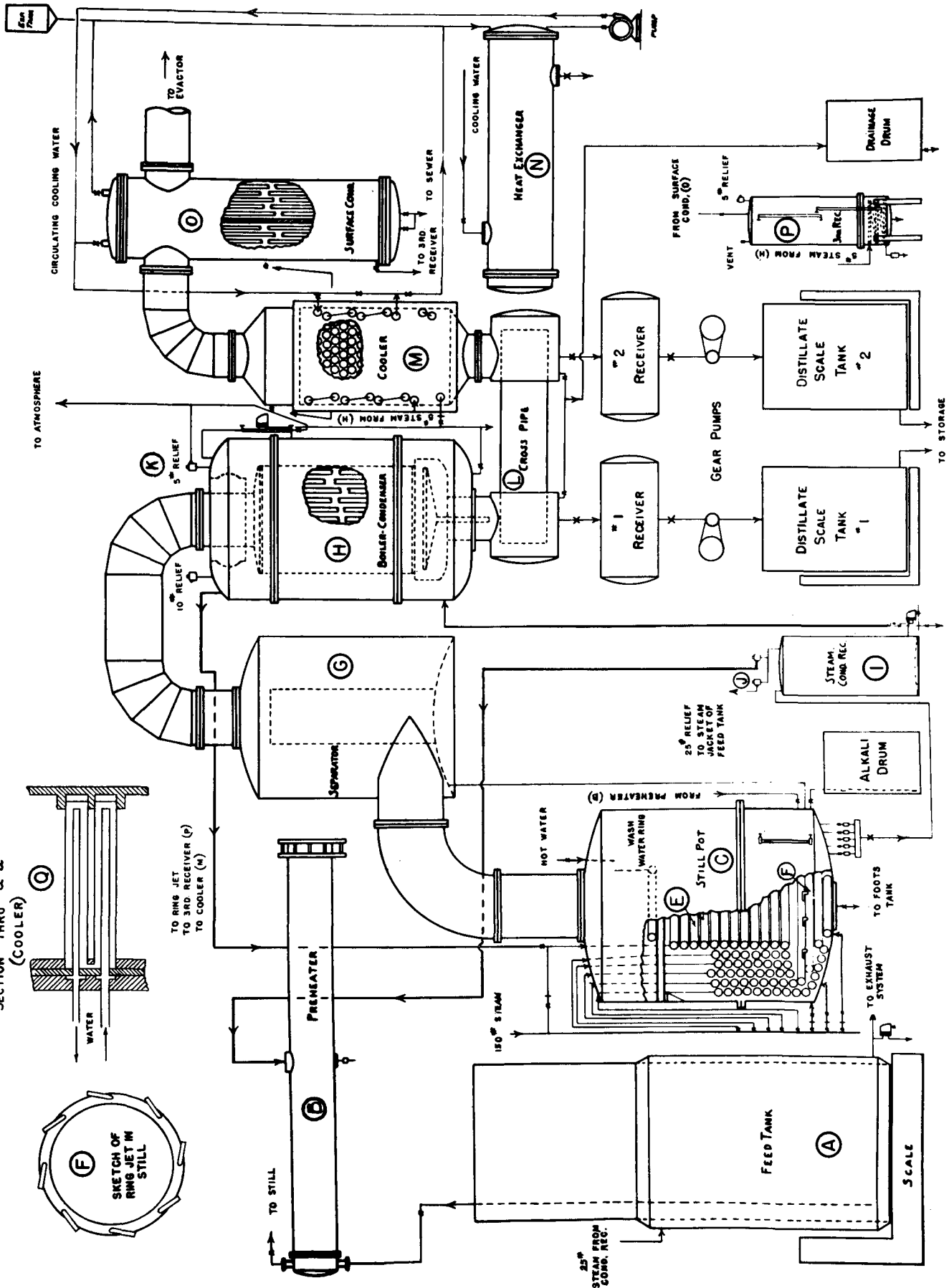


Fig. 8. Diagrammatic sketch—Ittner glycerine still.



over pipe (L) connecting the first and second condensers at the bottom. The second condenser (M) is also known as the "cooler" and is operated at a lower temperature. The cooling medium in this case is circulating water, which enters at the top at 90 to 100°F. and leaves the bottom at 180-190°F.

Here practically all of the remaining glycerin is condensed at a concentration of 99.0-99.2% glycerol. This fraction is used for "dynamite" or "high gravity" grade.

A final condenser (O) removes the last 1-2% of glycerin, at about 95% concentration. No sweetwater is obtained.

The total steam requirement is about one-third that of some older units. This is due to:

- Use of heat exchange to recover latent heat from the vapors
- Reduction of open steam requirement by use of high vacuum
- Elimination of sweetwater
- No redistillation required for U.S.P. grade
- No concentration of distillate required

### Bleaching

The fraction of the distillate intended for U.S.P. grade is bleached with activated carbon in order to remove the last traces of color and odor. The activated carbons possess a very high service absorbent efficiency so that the usual dosage required will be from a few tenths of 1% up to perhaps as much as 1% for the regular U.S.P. grade. For some special uses involving very rigid odor specifications, a somewhat higher dosage may be required.

The bleaching process is simple and requires nothing more than contacting the glycerin with the activated carbon at about 80-90°C. in a tank provided with an efficient agitator for about one-half to one hour. It is desirable to use stainless steel or aluminum tanks when glycerin is being bleached for U.S.P. For the dynamite grade little or no bleaching is required depending upon the color of the distillate and the quality of the crude from which the distillate was obtained.

The mixture is then filtered until crystal clear, using a small amount of diatomaceous earth if necessary to assist in clarification and to maintain a desired flow rate. The final step is to adjust the concentration as required by specifications. From the more modern distillation units glycerin will be obtained over 99% concentration, and water may be added to adjust it to the desired specification since no premium is paid for a higher concentration.

The finished glycerin is then put into tank cars, 55-gallon or 110-gallon drums, and 1-gallon and 5-gallon cans.

In order to avoid loss of glycerin in the carbon press cake from the filter presses it is customary to remove this cake and return it to the lye treatment tanks.

### Ion Exchange Purification (5)

In recent years the ion-exchange method has been developed to the point where it is being applied commercially (6). The advantages are that it eliminates the distillation step and that all of the glycerin can be U.S.P. quality instead of about 70% of it when distilled. The glycerin is also superior in some respects to that obtained by distillation.

The process is based upon the fact that when a non-ionizable substance, in this case glycerin, is contam-

inated chiefly by ionizable substances, in this case sodium chloride, sodium sulfate, fatty acids or soaps, certain insoluble resins have the properties of ion-exchangers—that is, a cation exchange resin will remove the sodium ions from the solution and replace them with hydrogen ions, forming hydrochloric acid, for example, from sodium chloride. By next passing the solution to an anion exchanger, the chlorine ions will be removed and replaced by hydroxyl ions, forming water.

Examples of the cation resins are:

Condensates of phenol sulfonic acid and formaldehyde  
Sulfonated polymers of styrene and di-vinyl benzene.

Examples of anion resins are:

Quaternized polymer of styrene and di-vinyl benzene (strong base)

Condensation product of aliphatic amines and phenol with formaldehyde (weak base).

Obviously, non-ionizable impurities such as polyglycerol, glycols, or esters would not be removed, but fortunately these normally exist only to an extremely small degree in the glycerin liquors, not enough to preclude the production of a high quality glycerin that meets U.S.P. specifications.

The process has been applied both to the purification of sweetwaters from the fat splitting process and to spent lyes from the kettle process. When sweetwater is to be handled, no prior evaporation is necessary since the impurities involved amount to only a few tenths of 1%. However, when spent soap lye is to be treated, the high salt content (10-15%) makes it necessary to evaporate as usual to an 80% crude to remove most of the salt in order to make the subsequent ion-exchange practicable. The crude must then be diluted to about 25-30% glycerol concentration in order to lower its viscosity enough to permit reasonable flow rates through the exchange vessels, after which the solution is re-evaporated to the desired concentration.

Naturally the economics are more favorable when sweetwater is to be purified, but it can be pointed out that commercial units are in operation on both sweetwater and soap lye crude. The solution to be purified must be free of fats and turbidity to avoid fouling of the resin beds. If these are present the solution is first filtered. Figure 9 shows a simple arrangement for sweetwater.

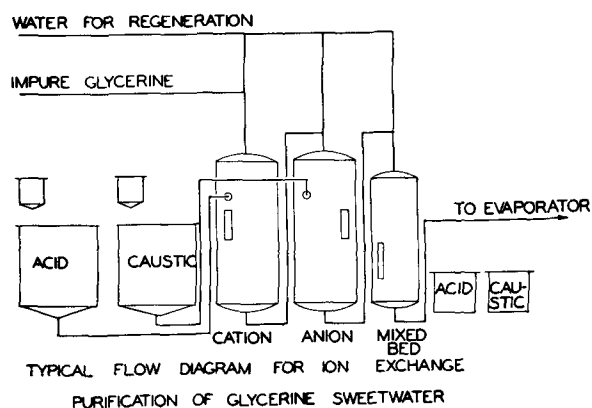


FIG. 9.

Courtesy of Illinois Water Treatment Co., Rockford, Ill.

Since a single pass through a cation and an anion exchanger is not 100% efficient, the process is designed to provide multiple passes in series; each succeeding pair of exchangers being smaller and sized so that all units will require regeneration at the same time.

The degree of purity required for the finished product and the quality of the starting material will govern the number of stages necessary. For sweetwater, one or two stages plus a mixed bed stage may be required, while for the purification of soap lye crude, three stages are used in series, plus a "mixed bed" as the final stage. This mixed bed is very efficient and removes the last traces of impurities. It contains both cation and anion exchange resins intimately mixed; therefore the effect is that of a great number of small individual units. For example, in a bed 24" deep there are theoretically 407 de-ionizers operating in series.

The operation of the process is simple. The raw solution is pumped, at about 95°F., through the units in series at the designed rate. The soap lye crude has been prepared by dilution to 25-30% glycerol and filtration. Since the resin beds are kept covered with water between operating cycles, the first effluent from the process will be displaced water, followed by dilute glycerin. In practice, the effluent is run to a separate tank until the glycerol concentration reaches 15%, at which point it is run to the product tank. The dilute solution is used as water for dilution of a succeeding batch of crude. This early phase is known as "sweetening on" a term borrowed from the sugar industry. At the end of the cycle the procedure is reversed while water is pumped through to displace the glycerin. This is known as "sweetening off."

The length of the cycle is governed by the amount of resins in the vessels in relation to the amount of solution passed through and the ionizable salts contained and is designed to fit the operating schedule desired. For example, the cycle illustrated here is 12 hours including purification and regeneration of the resin beds. The cycle is necessary because the resins become saturated with absorbed ions and must be regenerated.

Regeneration is accomplished in the cation exchangers by pumping a 12% solution of sulphuric acid through them. The sodium ions are converted to sodium sulphate. For the anion exchangers a 5% sodium hydroxide is used, and the corresponding sodium salt, such as sodium chloride, is formed. These solutions are discarded and the beds rinsed with water, after which the next cycle can begin.

In regeneration of the mixed bed it is first necessary to separate the cation and anion resins. This is

possible because the anion resin has a lower density and can be classified by backwashing the bed with water until the resins are separated into two layers, the anion resin on top of the cation resin. Regeneration is then accomplished by passing sodium hydroxide solution through a top inlet and sulphuric acid through a bottom inlet, drawing these off at the interface. After rinsing, the resins are remixed by air agitation.

The final operation is to concentrate the purified solution to the desired concentration, such as 95% glycerol for the U.S.P. grade. If this is done in a stainless steel exaporator, no bleaching is needed. All of the color is removed in the ion exchangers since some of the resins used have very good color absorbing characteristics.

### Production and Uses of Glycerin

The total domestic production of glycerin in 1951 was reported as 211 million pounds, of which 171 million was obtained from fats and oils.

Glycerin has literally many hundreds of diversified uses, the most important of which are:

a) As a chemical in esterification reactions. Since glycerin is a tri-hydric alcohol, it contains three functional hydroxyl groups and is utilized in the preparation of:

1. Alkyd resins, which basically are esters of glycerin and phthalic anhydride;
2. Ester gums, which are esters of glycerin and rosin;
3. Mono- and di-glyceride esters of fats and oils.

b) Because of its non-volatility at ordinary temperatures it is used as a plasticizer in cellophane, sausage casings, glassine, and grease-proof papers.

c) The hygroscopic properties of glycerin make it useful in tobacco as a humectant.

d) One of the oldest uses of glycerin is in the manufacture of the explosive nitro-glycerin, which is an ester of glycerin and nitric acid.

e) Glycerin has wide use as a solvent, moistening agent, and as a vehicle in pharmacy, food products, syrups, and cosmetics, such as skin creams and lotions, dentifrices, and shaving creams.

f) There are a host of other miscellaneous uses too numerous to mention here, based largely on the physical characteristics of glycerin, such as its high viscosity, low freezing point, hygroscopicity, non-volatility, pleasant taste, non-toxicity, solubility, solvent power, and stability to oxidation.

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