Since further work will be necessary to obtain agreement between collaborating laboratories and since several minor points such as the use of potassium iodide solution must be studied, no detailed report will be given at this time. Further work will be carried out as promptly as possible.

One disconcerting fact has been demonstrated by the present work. These same five oil samples have been studied by the Spectroscopy Committee and the Liquid-Solid Acids Subcommittee. The Spectroscopy Committee furnished iodine values on these oils with 8 out of 12 values for each oil in close agreement. Saturated acids have been measured by two laboratories on the linseed, soybean, and cottonseed oils by the crystallization procedure, and the results are in agreement. If these averaged values for iodine values and saturated acids are used, together with the thiocyanogen values as determined in this work, to calculate the composition of the linseed, soybean, and cottonseed oils, then composition are found which are not in agreement with those found by other methods of analysis such as the spectrophotometric.

The present work shows that much more work must be done before a satisfactory determination of the composition of vegetable oils can be made.

Stability Test

V. C. Mehlenbacher, Subcommittee Chairman

Progress this year on the Fat Stability Test has concentrated on the redesign of the apparatus which is now under construction. A report of results with this apparatus will be made available at another time.

Insoluble Impurities Determination

It was called to our attention during the year that some laboratories disliked using petroleum ether for washing the residue in the insoluble impurities determination. It was disliked because of the hazard involved. Several members of the Committee made a comparison between petroleum ether and carbon tetrachloride on a variety of fats. The results appear in the following tabulation:

Laboratory 14		Laboratory 13		Laboratory 6		Laboratory 12		Laboratory 4	
P.E.	C.T.	P.E.	C.T.	P.E.	C.T.	P.E.	C.T.	P.E.	C.T.
0.15	0.15	0.10	0.09	0.52	0.55	0.29	0.25	0.16	0.15
1.10	1.18	0.17	0.15	0.72	0.70	0.14	0.17	0.66	0.73
0.08	0.06	0.18	0.22	0.02	0.01	0.22	0.39	0.66	0.65
0.39	0.36	0.20	0.19	0.02	0.01	0.32	0.30	1.10	1.05
0.18	0.17	0.50	0.53	0.02	0.01	0.11	0.13	......	......
0.80	0.80	0.70	0.66	......	......	0.36	0.39	......	......
......	......	......	......	......	......	0.74	0.68	......	......
......	......	......	......	......	......	0.23	0.25	......	......
......	......	......	......	......	......	0.13	0.17	......	......
......	......	......	......	......	......	3.68	3.16	......	......
......	......	......	......	......	......	1.26	1.42	......	......
......	......	......	......	......	......	0.45	0.47	......	......

P.E.—Petroleum Ether.
C.T.—Carbon Tetrachloride

The above results indicate that carbon tetrachloride and petroleum ether are equally satisfactory. On the basis of these results the Committee recommends that carbon tetrachloride be permitted as an alternative washing agent for use in the insoluble impurities determination.

Analysis of Tall Oil

The agreement at the Committee meeting a year ago was to follow the progress of the A.S.T.M. in their development of methods for the analysis of tall oil. The activities of the A.S.T.M. during the past year have concentrated on other products so that no progress has been made in the case of tall oil.

E. W. Blank
E. W. Colt
F. G. Dollear
Jacob Fitelson
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C. P. Long
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H. A. Schuette
L. M. Tolman
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D. S. Bolley
L. R. Brown
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W. K. Hilty
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New Techniques in Glycerine Distillation*

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In recent years significant improvements have been made in distillation equipment and technique. Glycerine refiners have been aware of the need for modernized equipment in order to realize economies in consumption of fuel, to produce C. P. grade without resorting to multiple distillations, and to achieve economy of space by increasing the productive capacity per unit. "Sweetwater" produced in the older type stills was undesirable since these weak concentrations—ranging from 2.5-5.0% glycerol—had to be re-evaporated and redistilled, and even then the distillate was of poor quality, being rich in trimethylene glycol and saleable only as "Yellow Distilled." A further disadvantage of the older units was the necessity for concentrating the distillate up to 98.7%, the minimum standard for "Dynamite" glycerine.

The purpose of this discussion is to review some recent advances in solving these difficulties. More specifically, we will describe the design features and the operation of a distillation unit which has been used successfully in commercial operation for several years and which has not heretofore been described in the literature. Recognizing the need for improvements, Dr. M. H. Ittner was successful in designing a unit (now known as the "Ittner Still") which eliminated the undesirable features of the older stills, and which will be described here (1). Dr. Ittner touched upon it, but very briefly, at the time he received the Perkin medal in 1942 (2). An improved type of glycerine still has also been described by Wurster (3).

With the aid of the chart we can follow the sequence of flow. Beginning at the left we note the feed tank "A." This has a capacity of 20,000-25,000 pounds and is mounted on a scale (for accounting purposes) and is provided with a steam jacket for partial pre-heating of the crude. The crude is drawn into the still by means of a vacuum in the still system, first passing through the main pre-heater "B." This is a

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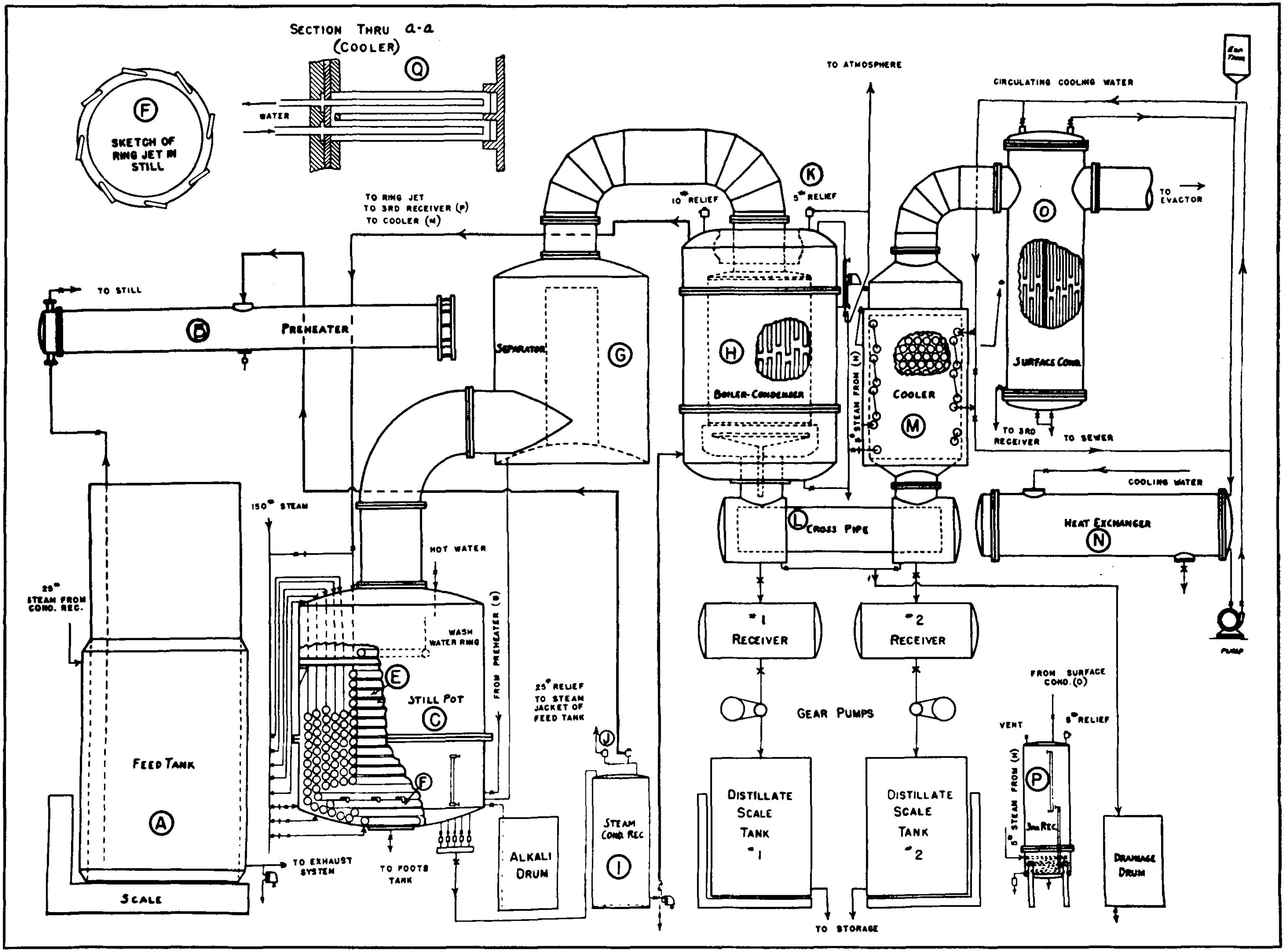
* Presented at the 20th annual fall meeting, American Oil Chemists' Society, Chicago, Oct. 30-Nov. 1, 1946.



Diagrammatic sketch—Ittner glycerine still.

tubular heat exchanger with 375 square feet of surface. Both pre-heater "B" and the scale tank steam jacket are heated by steam generated within the still system itself as will be more readily seen from the description to follow. The temperature of the crude is raised 80-100° F. in the pre-heater, and enters a nickel-clad still "C" at about 250° F. Here it is brought to distillation temperature (330° F.) by closed steam coils. There are five separate coils, made of nickel, having a total heating surface of 400 square feet and individually controlled for flexibility of operation. The large heating area, combined with the low pressure in the system (10-15 mm. absolute) make possible a rate of 1,100 pounds of distillate per operating hour with soap lye crude as the feed; the rate for saponification crude is 1,300 pounds per hour, and for redistilling lower grades of glycerine is 1,500 pounds per hour. The absolute pressure in the still is maintained by a three-stage steam evactor and a barometric condenser.

The open steam is admitted to the still through a central superheater coil "E" which enters at the top of the still and terminates near the bottom in a circular ring jet (see inset "F" for detail), from which eight separate tangential branch jets inject the open steam into the crude, setting up a very active circulation around and between the five banks of closed coils—thus obtaining a high heat transfer rate with very little superheating of the liquid. The jet steam is superheated by the glycerine vapor above the liquid level. The amount of open steam is controlled by an orifice plate and is entirely independent of the operator's judgment. The orifice size is calculated to deliver 0.25 pound steam per pound of glycerine distilled. Three supplementary open steam ring jets are provided, controlled by separate orifices. These jets are below the main open jet and are used only during the boildown at the end of a run when the level of crude falls below the main open steam jet, "F."

The vaporized glycerine passes through a centrifugal separator of the Weber type, "G," and here is freed of any entrainment. This type of separator is extremely efficient—the residual salts in the distillate are of the order of 2 ppm NaCl, 3 ppm Na_2SO_4, 1 ppm iron, and 0.001-.002% total ash. The mixture of pure glycerine and water vapor then enters the boiler condenser, "H." This vessel is a tubular heat exchanger designed to condensate approximately 70% of the glycerine vapor under constant controlled temperature.

At this point it is advisable to trace the flow of high pressure steam, condensate, and regenerated low pressure steam, which is one of the unique features of this unit. Referring to the chart, we note that all of the steam condensate from the closed coils flows through traps to a condensate receiver, "I." Here the pressure falls from 150 p.s.i. to 25 p.s.i.; in so doing, about 10% of the condensate flashes into steam. Two relief valves "J" on the condensate receiver feed this flash steam to various desired points. One relief valve discharges at 20 pounds and feeds the main preheater "B." The second relief valve is set at 25 pounds and takes excess flash steam first through the jacket on the scale feed tank "A," and finally to the 5-pound exhaust steam system. The condensate discharges from the bottom of the receiver at 20-25 pounds pressure and enters the boiler-condenser "H." Here its pressure again drops to 5 pounds, which is the constant pressure maintained in this vessel. Some flash steam is again created; the balance becomes the feed water for the boiler.

In this boiler-condenser a heat exchange takes place between the latent heat of the glycerine vapor and the water in the boiler-condenser, thus generating the low pressure steam for the open jet ("F") in the still. Some of this self-generated steam is used in other parts of the system—the concentrating tubes in condenser "M" and in receiver "P" as will be described later. At the start of a run high pressure steam is fed to the open coil for about 10-15 minutes, until enough glycerine vapor is distilling to raise the boiler temperature to a positive gauge pressure. As soon as a positive pressure is noted, even 2-3 pounds, high pressure steam is shut off and from here on the still generates its own open steam. The pressure in the steam boiler is held constant at 5 pounds by a relief valve, "K," thus maintaining a constant condensing temperature of 228° F. The water level in the boiler is held constant by an overflow trap discharging excess water to a hot water supply tank.

The mixture of vapor and condensed glycerine leaves the bottom of the boiler at 250-260° F. and enters the cross pipe "L" which separates the vapor from the liquid—allowing the liquid to flow into receiver No. 1. Approximately 70% of the glycerine is condensed at this point and is 99.5-99.8% concentration. From normal quality crudes the color of this distillate will average 1.5 Yellow - 0.5 Red (5¼" Lovibond Cell) and requires only bleaching to bring it up to U.S.P. quality. All parts of the boiler, cross pipe, and first receiver which come in contact with C. P. glycerine are stainless steel.

The remaining glycerine vapor and all of the uncondensed water pass through the cross pipe and enter the cooler "M" at the bottom. The cooler is a tubular heat exchanger containing 16 rows of horizontal tubes, arranged so that the cooling water flows downward countercurrently to the vapor (see inset "Q" for detail). In this vessel practically all of the remaining glycerine, but almost no water, is condensed. Here again the condensing temperature is controlled by the temperature of the water flowing through the tubes. The lowest row of tubes is the hottest, thus condensing the least amount of water and further serving to remove excess water from the cooler glycerine flowing down over the tubes from the upper part of the condenser. The circulating cooling water enters the top row of tubes at 90-100° F. and leaves the bottom row at 180-190° F. This heat is removed by a separate heat exchanger "N," using river or well water as the ultimate cooling medium. The internal circulating system may be inhibited to minimize corrosion since this vessel condenses the glycerine normally used for "Dynamite" grade and the tubes are of steel construction.

Twelve of the 16 rows of tubes are connected to the circulating water system; the four bottom rows are heated by the 5-pound steam generated in the boiler-condenser "H," the amount being controlled by an orifice. This serves to insure high concentration in the distillate by re-evaporation of any small amount of water in the glycerol condensate, which must flow over these hot tubes before entering the No. 2 receiver. The condensed and concentrated glycerine then flows down the far end of the cross pipe and into the second receiver; its concentration is 99.0-99.2% glycerol. This 30% fraction may be used for commercial "High Test" or "Dynamite" grades. From normal crudes its color will average 4.0 Yellow - 1.5 Red (5¼" Cell) and can be reduced to almost water-white by bleaching if desired.

The water vapor leaves the top of the cooler at 150-160° F. and passes through a surface condenser, "O," where the remaining 1-2%, a mixture of glycerol and glycols, condenses and flows into a small receiver, P." Any condensed water is re-evaporated in this receiver by a small closed coil supplied by 5-pound steam recovered from the boiler-condenser. The small fraction of distillate recovered here is 95% or higher in glycerol. The water vapor leaves condenser "O" at 110-120° F. and passes to the barometric condenser.

From the small receivers, Nos. 1 and 2, which have a capacity of about 400 pounds each, the distillate is removed either continuously or periodically by small gear pumps to scale-mounted receiving tanks. The advantage of scales for both the crude and the distillates is obvious to anyone who has been faced with the problem of investigating "unknown" losses which occur from time to time in any glycerine plant.

The advantage of dispensing with large distillate receivers attached to the still system is obvious; time is saved at the start of the run, since there are no receivers to evacuate. In fact, the unit can be brought to on-stream distillation conditions in about 20 minutes.

Although the Ittner still has been operated mainly as a batch process, it can readily be adapted to continuous operation by the installation of a salt receiver attached to the bottom of the still, from which the slurry can be blown to an agitator feed tank, followed by centrifugal separation of the liquor and salt, with subsequent return of the liquor either to the main still or accumulation for separate boildown. It is obvious that in the distillation of salt-free crude, such as that resulting from the fat splitting process, continuous operation would be more readily achieved since there is no salt to contend with.

The over-all yield obtainable depends primarily on the method of handling foots. In most plants where this unit has been used facilities for subsequent treatment of the foots were available, in which case the charge in the still at the end of the run was boiled down to a foots amounting to 4-5% of the glycerol originally fed. This residue was dissolved in hot water in the still and sent to the foots treatment department, resulting in a final foots discard of 2.0-2.5%. By the use of salt receivers and centrifugal separation, foots treatment can be dispensed with and the foots of 2.0-2.5% could be obtained by direct boildown after the liquor has been freed of salt. The "unknown" disappearance during distillation should not exceed 0.5%, thus making a total yield of 97-98%.

The small fraction (1-2% of total distillate) condensed in the final condenser will contain some trimethylene glycol (5-10%); this material can be accumulated and fractionated to separate the trimethylene glycol from the glycerol. By the isolation of this fraction no impurities are re-cycled, thus creating a so-called "open system." There will be practically no trimethylene glycol in the "Dynamite" fraction, as indicated by its high concentration derived from specific gravity analysis. The specific gravity of trimethylene glycol (1.054) is so close to that of water that its presence is readily revealed by the specific gravity analysis.

Steam Economy. The total steam consumption is 2.25 pounds of steam per pound of distilled product. For saponification crude, the over-all factor is 1.9 pounds steam per pound of distillate. The breakdown of steam consumption is as follows (pounds steam per pound of distillate):

Coil steam	0.85
Steam to operate vacuum apparatus	1.15
Steam for washing out stills, etc	0.25
Total	2.25

On the older type units the steam consumption was between 7-8 pounds. This reduction of 70% in steam consumption amounts to approximately $7,000 per year per still unit when used at capacity. Steam economy is made up of the following factors:

1. Recovery of most of the latent heat in glycerine vapor to generate the open steam used by the still.
2. Reduction in the amount of open steam required. On the older type units the common practice was to use about 1.5 pounds of open steam per pound of glycerine distilled; this was all live steam. In the newer units, due to operation at lower pressures, the amount of open steam required varies between one quarter and one third of a pound per pound of glycerine distilled and is generated within the system.
3. No re-distillation is required for C. P. glycerine.
4. There is no sweetwater to be re-evaporated.
5. No concentration is required for any of the distillate.

Quality Advantages. 1. Seventy per cent of the distillate is suitable for C. P. grade, if crude of normal quality is used.

2. On account of the very light color of the distillates produced economies are obtained in the use of activated carbon for bleaching.

3. The more complete removal of trimethylene glycol by its isolation in the third receiver fraction gives a purer grade of "High Test" or "Dynamite" glycerine and permits further recovery of the trimethylene glycol as a valuable by-product.

4. No undesirable impurities are re-cycled.

Capacity. The distillation rate of such units is 2-3 times the rates obtained on some of the older units; conservatively, one unit is capable of handling approximately 7 million pounds of crude per year.

Operation. A brief description of the operation may be of interest.

Prior to distillation a few prerequisites to good practice should be recognized. First, it is advantageous to maintain the concentration in the finishing evaporator as high as practicable. For soap plant operation, where the refiner produces his own crude, a minimum standard of 82% glycerol is suggested; a good practicable average is 83-85%. During distillation more than twice as much steam is required to distill excess water as to distill an equivalent amount of glycerol; this water can be removed in the evaporator, where in many cases exhaust steam is available. The vapor pressure of glycerine at the temperatures ordinarily employed in finishing evaporators is so small as to be negligible insofar as contributing to vapor loss is concerned.

It is generally recognized that sufficient time should be allowed for settling of the crude to remove mechanically suspended salt. A three-compartment storage tank has been found very satisfactory for presettling, each compartment having a capacity of one day's crude production. By rotating these compartments so that compartment No. 1 is receiving freshly produced crude, No. 2 is settling, and No. 3 is being used to feed the stills, a settling period of over twenty-four hours is assured. This has been found to be ample for settling *suspended* salt. The solubility of salt in glycerol is about 7% and varies little with temperature; therefore there is no appreciable gain in cooling the crude.

Crude should be adjusted to an alkalinity equivalent to 0.15-0.20% Na_2O in the form of caustic soda. This is usually added to the scale tank, which is provided with an air coil for agitation, and is done prior to distillation and is supplementary to the main alkali dosage added directly to the still.

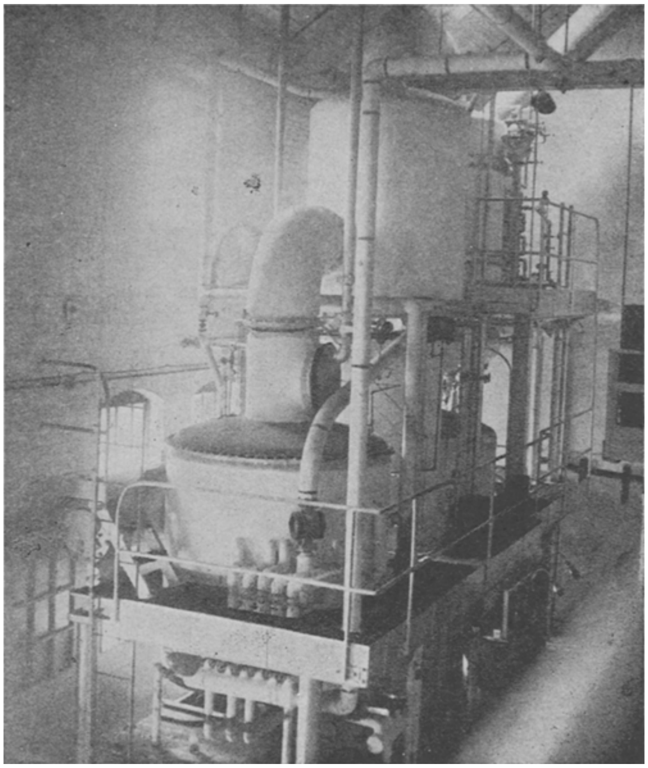
Control of the fatty acid-ester content of the distillate is accomplished mainly through alkali dosage in the still itself. Either caustic soda or soda ash can be used, with little effect on the degree of polymerization. Caustic soda is more effective than soda ash but is slightly more expensive; the added expense, however, is offset to some extent by the greater ease of handling as 50° Baumé liquid caustic. Depending on the quality of the crude, an initial alkali dosage of 1-3% Na_2O based on the initial still charge is added to the still at the start of the run and no further additions are made. The advantage in adding the alkali in this manner is that a higher concentration of caustic in the glycerine that is actually being distilled at any moment is maintained without increasing the over-all usage. Since the initial charge is 2,500 pounds, the dosage of 50° Baumé (38% Na_2O) caustic soda will average between 100-200 pounds. The fatty acid-ester content of the first receiver distillate will run between 0.010-0.020% Na_2O—well below the U.S.P. specifications.

The crude in the scale tank (after adjustment of alkalinity) is agitated with air, sampled, and weighed. The vacuum apparatus is then put in operation and as soon as about 10″ vacuum is present, crude will begin to flow into the still. The pre-heater is by-passed at the start, since there is no flash steam being generated.

As soon as crude starts to enter the still, all five closed coils are turned on full. When the crude level shows in the gauge glass, high pressure steam is turned on the main open jet "F" and the pre-determined charge of alkali is fed to the still from a drum underneath. As soon as the crude reaches normal operating level (midway in the gauge) the pre-heater is put into operation, using flash steam from the condensate receiver. As soon as distillation starts, as evidenced by the development of a positive pressure in the boiler-condenser, high pressure steam is shut off coil "F" and low pressure steam from the boiler-condenser is turned on.

During all the foregoing operations the pressure in the system continues to fall rapidly so that by the time distillation begins, the normal operating pressure of 10-15 mm. is reached. In about 20 minutes from a "cold start" glycerine begins to appear in the receivers.

A constant operating level in the still is easily maintained by means of a smaller by-pass feed line, controlled manually. Since all steam flows are orifice-controlled, very little operator attention is required after on-stream conditions are established.



Typical installation—Ittner glycerine still.

As distillate collects in the receivers, the gear pumps transfer it to the final distillate scale tanks. These tanks hold the distillate from an average run, at the end of which the glycerine is weighed and sampled before transfer to bleaching.

For batch operation the feed is stopped after 20,000 pounds of crude have been fed. Distillation is continued until the level falls below the main open jet "F." At this point, "F" jet is shut off and the three open ring jets are all turned on full. Again, orifices control the amount. The "boildown" is continued until virtually no glycerine is being condensed.

The still is then shut down and the residual foots dissolved by adding water to the still and boiling. An auxiliary vacuum jet is provided to draw vapors directly out of the still head and to prevent such vapors entering the condensing system. The dissolved foots is sent to the foots treatment department for secondary recovery.

As mentioned earlier, foots treatment can readily be eliminated by semi-continuous removal of salt during distillation, which would in addition permit continuous operation of the still itself.

Summary. A new distillation unit, having high capacity and high steam efficiency is described. C. P. glycerine of high purity is obtained in one distillation. The features of the still include generation of open steam for distillation within the still system by recovery of latent heat from glycerine vapors. Extremely high concentration of final distillate is obtained by controlled condensing temperatures and low absolute pressure in the system. Countercurrent condensation of the final vapors results in very efficient "scrubbing" of the glycerine from the vapors, including the re-evaporation of any condensed water. Isolation of any undesirable distillation products, such as trimethylene glycol, is improved. The color of the distillate is improved so as to require little bleaching. The fatty acid-ester content of the distillate is under positive control. Additional unusual design features are:

Two-stage pre-heating of the crude by steam recovered from condensate.
Distilled water for the "boiler-condenser" is assured by use of steam condensate.
Continuous distillation is possible.
Sweetwater is entirely eliminated.
No closed distillate receivers are required.
Separate concentration of distillates is eliminated.

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3. "Glycerine Distillation," by O. H. Wurster; Oil & Soap, Volume XV, No. XI, p. 292, November, 1938.

Computation Forms Relating to the Component Acid Analysis of Marine Animal Oils by the Ester Fractionation Method

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In the ester fractionation procedure (1) for the component acid analysis of natural fats the compositions of the individual fractions are calculated from their determined saponification equivalents and iodine values. With marine animal oils in particular these calculations can be laborious and time-consuming, and we have found the elaboration of definite computation forms of very great assistance; once set up, they enable the compositions of most fractions to be calculated with the assistance of a computor. Moreover the use of such tables provides a concise and permanent record of the computations and great facilitates checking of calculations. In the present communication we therefore record such computation schemes as have been employed in recent component acid analyses of marine animal oils carried out in this laboratory (2). All have been arranged so as to make efficient use of tables of reciprocals, of multiplication tables such as those of Crelle (3), and of computing machines.

Computations relating to fractions containing two saturated plus two unsaturated esters:

The early "solid" and "liquid" ester fractions have been calculated to one or other of the following:

(a) C_{12} and C_{14} saturated plus monoethenoid esters;
(b) C_{14} and C_{16} saturated plus monoethenoid esters;
(c) C_{16} and C_{18} saturated plus monoethenoid esters.

In calculating to these compositions, it has been customary in this laboratory to assume that the S.E. of the saturated portion of each fraction is the same as that of the whole fraction. This assumption leads to little error in the final analysis and does away with the necessity for isolating the saturated ester fraction. The compositions of such fractions may therefore be calculated from equations (1)-(3)

$$x + y + z = w \qquad (1)$$

$$\frac{x}{E} + \frac{y}{E_1} + \frac{z}{E_2} = \frac{w}{E} \qquad (2)$$

$$i_1 y + i_2 z = wi \qquad (3)$$

where w = the weight of the fraction, whose S.E. = E, and I.V. = i.

x = the weight of the saturated C_n plus C_{n+2} esters in the fraction, whose S.E's. E_3 and E_4 are equal to $(E_1 + 2)$ and $(E_2 + 2)$ respectively.

y = the weight of C_n monoethenoid esters of S.E. = E_1 and I.V. = i_1 in the fraction.

z = the weight of C_{n+2} monoethenoid esters of S.E. = E_2 and I.V. = i_2 in the fraction.

The solutions to these equations (1)-(3) are given in equations (4)-(6):

$$z = \frac{wi}{i_1} \cdot \frac{1}{Q + \frac{i_2}{i_1}} = \frac{wi}{i_1} \cdot \frac{1}{Q + \frac{E_1}{E_2}} \qquad (4)$$

since both series of unsaturated esters are monoethenoid and therefore $\frac{i_2}{i_1} = \frac{E_1}{E_2}$

$$y = Q \cdot z \qquad (5)$$

$$x = w - (y + z) \qquad (6)$$

where $Q = \frac{E_1}{E_2} \cdot \frac{E_2 - E}{E - E_1}$

The composition of the saturated ester fraction x may be calculated from the equations (7) and (8):

$$u + v = x \qquad (7)$$

$$\frac{u}{E_3} + \frac{v}{E_4} = \frac{x}{E} \qquad (8)$$

the solutions to which are

$$u = \frac{b - d}{c - d} \cdot x \qquad (9)$$

$$\text{and } v = \frac{c - b}{c - d} \cdot x \qquad (10)$$

where u = the weight of C_n esters of equivalent weight $(E_1 + 2)$ present.

v = the weight of C_{n+2} esters of equivalent weight $(E_2 + 2)$ present.

$$c = \frac{1}{E_3} = \frac{1}{E_1 + 2}$$

$$d = \frac{1}{E_4} = \frac{1}{E_2 + 2}$$

$$b = \frac{1}{E}$$

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