

The same method may be used for the estimation of vapor pressures from boiling points only. We shall illustrate, however, by a hydrocarbon the vapor pressure curve of which is known, *i. e.*, calculate the vapor pressure of toluene from its boiling point, 110.4° C., in order to be able to compare the result with the experimentally determined vapor pressure.

The equation used to find the heat of vaporization in the previous examples serves here.

$$\frac{\Delta T_w}{\Delta T} = \frac{L}{L_w} \left( \frac{T_w}{T} \right)^2 = \text{Slope of } (T_w - T) \text{ curve.} \quad (1)$$

The value of  $L$  in this equation may be obtained from the preceding article (Plot 3).

$$\frac{1000p}{T} \text{ in this case equals } \frac{1000 \times 1}{383.4} = 2.62$$

The value of  $\frac{L}{T}$  corresponding to 2.62 from Plot 3, using the calculated curve, is 22.6, whence,

$$L = 22.6 \times 383.4 = 8650.$$

Substituting this value of  $L$  in Equation 1,

$$\frac{\Delta T_w}{\Delta T} = \frac{8650}{18.02 \cdot 542.6} \times \left( \frac{373}{383.4} \right)^2 = 0.841$$

$$(100 - t_w) = 0.841 (110.4 - 90)$$

$$t_w = 82.8^\circ.$$

This means that at 82.8° C. water will have a vapor pressure equal to that of toluene at 90° C. This makes the vapor pressure of toluene 398 mm. at 90° C. Landolt-Börnstein gives a value of 405 mm. for 90°.

If the above calculations are repeated, using for the heat of vaporization of toluene the value given by Landolt-Börnstein, 7990 at 110.4°, we get a value of 420 mm. for the vapor pressure of toluene at 90° C.

It was by calculations the reverse of the above that all the points on the dotted curve of Plot 3 of the preceding article were obtained. In calculating vapor pressures of hydrocarbons one should therefore use the dotted curve of that plot.

While it is true that these equations assume that the gas laws apply to the vapor, if the vapors, both of the unknown liquid and of the liquid of reference, deviate in the same direction and to the same extent from the gas laws, the value of  $R$  for the two vapors will be identical and the relationship between the two liquids will be accurately expressed by Equation 3. As a matter of fact, liquids have a tendency to deviate in the same direction from the gas laws, and at low pressures this method of calculation will give results as accurate as much of the experimental data in the literature.

As pointed out by Johnston, it is usually possible to find a liquid of reference which will give a line nearly straight, but it is easier to use water and to measure the actual slope at the point in question because all the properties of water are accurately known and available.

Referring to the plot of the preceding article, it will be noticed that the heats of vaporization of the hydrocarbons as calculated by this method (shown by the dotted curve) deviate from the experimental values when  $P/T$  is high. When  $P/T$  is low, the agreement is excellent. This is probably due to deviation of hydrocarbon vapors from the gas laws, even below atmospheric pressure.

#### NOMENCLATURE

- $L$  = Molal heat of vaporization.  
 $p$  = Vapor pressure of the liquid under discussion.  
 $R$  = The gas constant.  
 $T$  = Absolute temperature in ° C.  
 $t$  = Temperature in ° C.

#### SUMMARY

A method of estimating the vapor pressure of a liquid at any temperature, one point on whose vapor pressure curve is known, is presented, and a method of getting heats of vaporization from vapor pressure data by a consideration of the Clausius equation is pointed out.

## Present Practice of Dynamite and Chemically Pure Glycerol Distillation

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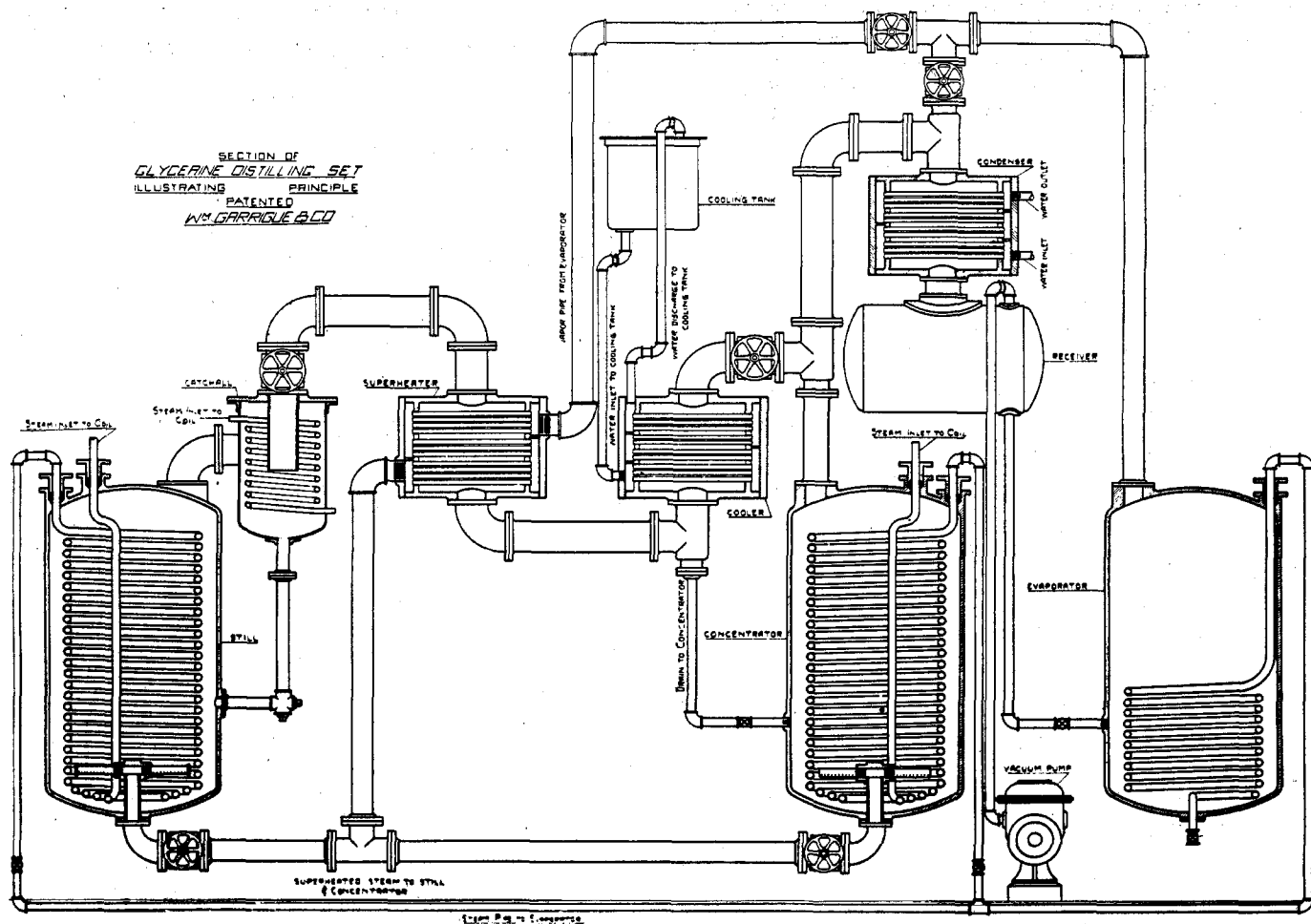
THE equipment and process used in recent glycerol distillation practice are interesting not only as applied to glycerol distillation but also as representing possibilities in distilling other products, particularly those liquids which show a tendency to decompose partly when distilled directly or alone at normal pressure. As an industrial process eliminating waste and conserving heat energy, modern practice in glycerol distillation is a good example of chemical engineering efficiency.

The principle of operation of glycerol distillation is illustrated in the diagrammatic cut in Fig. 1. By following the vapor piping system, it is plain that the system utilizes the double effect or heat regenerator principle used in multiple effect evaporation. This principle is made use of by injecting into the still, instead of steam, the vapor from evaporating weak glycerol water (called sweetwater) and by superheating this vapor with the hot glycerol vapor from the still.

#### APPARATUS<sup>1</sup> AND PROCESS

The crude glycerol in the still is heated by means of a continuous closed steam coil, and the vaporized glycerol is distilled over in an atmosphere of superheated water vapor issuing from the perforated spider shown in the illustration. The vapors from the still enter the superheater or heat exchanger where most of the glycerol condenses on the copper tubes. In doing this, there is a transfer of sensible heat as well as latent heat of condensation to the water vapors inside the tubes which are on their way to the spider in the still. The glycerol condensed in the superheater drops into the concentrator. The uncondensed glycerol vapors pass to the cooler or first surface condenser, where the temperature is so regulated with warm water supply that practically all of the remaining glycerol is condensed and removed to the concentrator, while the uncondensed steam vapors, with a small per cent of glycerol vapor, continue on to the final or sweetwater condenser. It will be understood that temperature control of the water in the cooler condenser is regulated so as to allow very little glycerol to enter the final surface condenser. In the final or sweetwater condenser, as it is called, complete condensation of vapors is effected with cold water in the tubes, and the condensate flows by gravity to the evaporator where it is continually being boiled by means of either a closed heating coil or a calandria steam chest designed much after the manner of the usual vertical tube calandria evaporator. The source of heat supply to the calandria or coil in evaporator may be either the exhaust from the still coil or an outside boiler supply. Vapor resulting from the boiling in the evaporator is carried through the superheater or heat exchanger to the still spider, and any

<sup>1</sup> Patented March 9, 1921, Serial No. 450,998, William Garrigue & Co.



glycerol carried beyond the cooler is again accumulated in the evaporator.

A constant vacuum is maintained throughout the entire system by a high duty dry vacuum pump connected to the receiver under the final condenser.

The rate of distillation is controlled by a valve supplying steam to the evaporator calandria or coil. The glycerol in the concentrator is maintained or brought up to desired specific gravity by controlling the steam supply to its coil. Water evaporated from the concentrator passes through a vapor outlet to the sweetwater condenser. In practice, the equipment is so constructed that any trimethyleneglycol originally present in the crude glycerol is driven from the concentrated charge by open steam injection. As a rule, however, unless the crude glycerol is unusually low grade, very little impurities will accumulate in the concentrator, but, on the other hand, will be collected in the evaporator. Provision is made for the separation of impurities accumulated in the evaporator by means of usual process of fractionation, the evaporator, condenser, and receiver being operated as a separate unit for this work.

Before placing a plant in operation, the vacuum breakers and other valves on the various units of equipment are closed and the vapor valves opened. The vacuum pump is then started and this is so connected as to draw vacuum on the entire equipment. As soon as the vacuum has reached the desired height, the crude glycerol feed line to the glycerol still is opened and the still filled until 3 or 4 in. of crude glycerol show in the gage glass.

The next step is to feed fresh water to the sweetwater evaporator until 6 or 8 in. show in the gage glass. After this is done, high pressure steam, preferably 150 lbs. gage at the still, is turned into the closed still coil. It is important that this coil be kept free from water so that it will at all times be under steam pressure. It is not difficult to maintain this condition if the valve on the still coil discharge is properly regulated.

Following this, a small amount of steam is turned into the evaporator closed coil or calandria. This is regulated so that the water in the evaporator will begin to boil at the time the crude glycerol reaches the distilling temperature. By this time, the vacuum pump will have reached maximum vacuum obtainable on the distilling system. The vacuum gage should register within 1 in. of the barometer reading.

There is perhaps more danger of priming the still at the beginning of operation than at any other period because if the glycerol is fed into the operating level of 3 or 4 in. showing in the gage glass and closed steam turned on with the vacuum too low, the distillation will start; under these circumstances it is very easy to carry over crude glycerol beyond the catchall, thus contaminating dynamite glycerol in the concentrator.

As pointed out above, when the water in the evaporator begins to boil, the vapors pass through the superheater condenser tubes and are then injected into the crude glycerol in the still through a special spray. In passing through the superheater, vapors from the evaporator are superheated by hot glycerol vapors which surround the superheater tubes. This exchange of heat between the high temperature vapors

from the still and the low temperature vapors from the evaporator results in the condensation of glycerol which passes with the flow of uncondensed vapor into the receiver and drops from the receiver into the concentrator.

Uncondensed glycerol vapors which have passed the superheater or heat exchanger, as it may be termed, pass on to the second condenser, which is termed a cooler condenser. The water supply to this second condenser is regulated so that practically all of the glycerol is condensed, but under the vacuum maintained on the system, little of the steam vapors are condensed. The glycerol recovered from the cooler passes to the second receiver and from there flows by gravity to the concentrator. From the second receiver the vapors containing only slight traces of glycerol pass to the final condenser, which is operated cold and condenses all remaining steam and glycerol vapors. This condensate, or sweetwater as it is called in practice, drops into the third receiver from which it flows by gravity to the sweetwater evaporator. From there it is again introduced into the still in the form of superheated water vapor, thus completing the cycle.

In practical operation, the still is given all the injection it will take from the evaporator without causing it to prime or to give a salty distillate. A sample of the liquor passing to the concentrator is taken from time to time and tested for salt.

It is apparent that an increase in the amount of steam to the evaporator coil will cause a fall in the vacuum in the evaporator due to the more rapid generation of steam. The point necessary to watch in this connection is that the vacuum does not fall so low that the sweetwater in the receiver under the final condenser will not flow to the evaporator. The difference in vacuum between the evaporator and the still is limited by the difference in height between the liquor in the sweetwater receiver and the liquor level in the evaporator. An operator readily learns how much he can open the valve on the steam line to evaporator closed coil or calandria so as to secure the proper amount of water vapor injection in the still and at the same time maintain the necessary relative vacuum between the evaporator and the still.

While the above operation is going on, high gravity glycerol liquor is accumulating in the concentrator. When this shows in the lower gage glass of the concentrator, steam is turned into the concentrator closed coil, care being taken at the beginning not to force evaporation, as this might reduce the vacuum on the entire system.

Water evaporated from the concentrator passes through the final condenser and thence into the sweetwater receiver to be returned to the evaporator. After glycerol accumulates in the concentrator and becomes more concentrated, the temperature will rise to about 250° F. This temperature drives most of the water off as rapidly as it runs from the first and second receivers, so that there is no difficulty in finishing to the required specific gravity for dynamite glycerol (1.262 at 15.5° C.) while the still is being cleaned out and prepared for the next run. The concentrator charge is usually considered finished when the temperature rises to 340° F. under full vacuum.

After the plant has been in operation about 0.75 hr., it will be found, if conditions are normal, that the glycerol liquor running to the concentrator will test between 25°-28° Bé., while the sweetwater returning to the evaporator will test less than 1° Bé. Under these conditions, the maximum amount of glycerol is going to the concentrator to be made into dynamite grade.

The still may be fed constantly or intermittently. In any event, care must be taken not to carry too high a liquor level in the still. Three or four inches in the gage glass is considered a good operating level. After the plant is well

started, the glycerol level in the still is the only point which requires much attention.

It is general practice to wash the still out once a day. The last feeding to the still should be made so as to allow sufficient time for the still to run down to foots before stopping the distillation to wash out. It requires on the average about 2.5 hrs. time to distil glycerol foots to dryness from an operating level of 3 in. in the gage glass. The actual time required depends upon the quality of the crude, the amount fed to the still, and the degree of dryness desired. If the foots are to be run to the sewer, running down to dryness is an important detail of the operation. An experienced operator soon learns the exact length of time to allow for finishing foots, depending upon the character of material he is handling.

After the foots have been finished properly, steam is shut off from the coils of the still and evaporator, and the vapor valve at the catchall closed. The valve on the line from the sweetwater receiver to the evaporator is also closed. Then the valve on the line from the receivers to the concentrators is closed so as to prevent any liquor which might remain in this line from running to the concentrators and diluting the finished glycerol. This done, the still and the evaporator are completely cut off from the rest of the equipment and the glycerol in the concentrator may be finished, that is, boiled down to the proper specific gravity while the still is being washed out. The vacuum breaker on the sweetwater evaporator is then opened. In doing this, the vacuum on the still is broken through the perforated cross. It is important that the vacuum on the still be broken through the sweetwater evaporator, because if broken by means of the vacuum breaker on the still catchall, the foots are drawn through the injection pipe back into the evaporator and might plug up this line. After the vacuum is completely broken, the vacuum breaker valve on the still catchall is opened and the sweetwater evaporator emptied. This sweetwater may be concentrated to a glycerol which is known as yellow distilled glycerol, or may be returned to dilute glycerol liquors and concentrated with them in a crude glycerol evaporator.

In washing out the glycerol still at the end of a run, only a little water should be run in at first; otherwise, because of the high temperature of the foots and still coil, steam pressure may be generated which would have a tendency to spring the still joints and cause leakage. In order to avoid this, care should be taken that the vacuum breaker on the still is open. As soon as pressure on the still is relieved after introduction of the first wash water, more water is run into the still and steam turned into the coil, leaving the coil drain valve open. The wash water is brought to a boil and the still washed out. In some cases the upper portion of the closed coil in the still is washed out by introducing water from a perforated pipe placed above the coil. If the glycerol foots are to be wasted, the first wash water should be enough to show in the gage glass. This dilutes the foots sufficiently so that the liquor is readily pumped. After boiling for a few minutes, the water is drawn off and the operation repeated until the still is thoroughly cleaned.

If the glycerol foots are to be saved, they are not distilled to complete dryness. Before dropping into the foots tank, several inches of water should be placed in the foots tank, as otherwise the foots will stick to the tank and give trouble in getting into solution.

After the glycerol in the concentrator has been brought up to the proper specific gravity, the concentrator is emptied and the distilling system made ready for the next run.

The finished dynamite glycerol from the concentrator is pumped to the glycerol receiving tank where a small amount of bleach is added. The amount of bleach used varies with character of stock distilled and the color required in the fin-

ished product. As a general rule, 1 lb. of bleach per 1000 lbs. of glycerol is used. On a good grade of dynamite glycerol it is only necessary to clarify the finished product. The glycerol, together with the bleach, is circulated from the receiving or bleaching tank through a filter press back into the receiving tank. This operation is continued until the glycerol is sufficiently clear for the desired purpose. The finished glycerol is then run into a drumming tank and either drummed or put in other suitable receptacles ready for shipment.

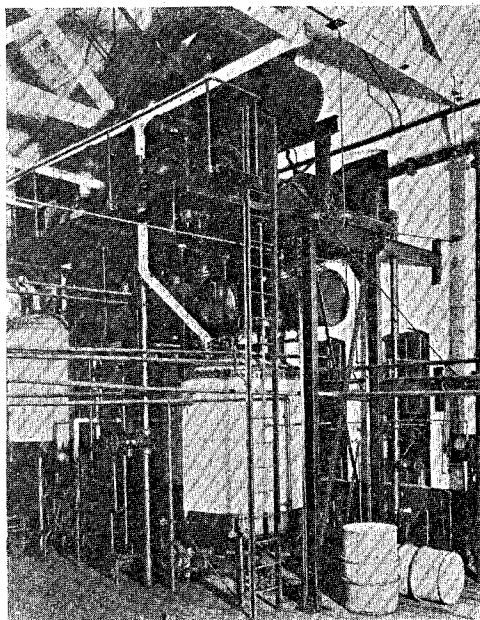


FIG. 2

The above gives us in brief the operating cycle in the production of dynamite glycerol in a typical modern glycerol distillation plant.

### C. P. GLYCEROL

The principle of operation is the same in the production of chemically pure glycerol. For this work a double unit distillation plant is usually installed. An illustration of this plant is given in Fig. 3. One side of this distilling plant operates continuously in the production of dynamite glycerol, while on the other side the dynamite glycerol is redistilled for the production of chemically pure grade. If the crude glycerol as fed to the dynamite still is sufficiently pure, chemically pure grade can be produced by redistillation only. In other cases, it is necessary to give the glycerol liquors an intermediate treatment between the dynamite and C. P. stage. In some cases this treatment consists of diluting, giving a lime treatment with subsequent concentration and redistillation, while in other cases the diluted dynamite glycerol is treated with zinc shavings in the presence of weak hydrochloric acid. Nascent hydrogen produced in this way in the glycerol liquors has a pronounced bleaching effect. Dynamite glycerol after being treated in this manner is again concentrated and redistilled.

There is no measurable loss in the operation of a glycerol distillation plant as described above with steam pressure at 150 lbs. The practical loss depends upon the disposition of the foots. If these foots are treated for the recovery of their glycerol content as crude glycerol and repeatedly returned to the still, there will be obtained a full yield of refined glycerol.

The percentage of glycerol in the foots depends upon the quality of the crude with special reference to the content of

total nonvolatile matter. Further, as pointed out above, it depends upon the disposition to be made of the foots how dry it is desirable to distil them. Nonvolatile residue will vary from 10 to about 15 per cent in the crude. The distillation can be carried to a point where this will retain as high as 25 per cent of its weight of glycerol, or if the crude contained 10 per cent of nonvolatile matter and 85 per cent glycerol, there would be 2.5 lbs. pure glycerol remaining in the foots per 100 lbs. of crude, or about 3 per cent of the total glycerol present. With ordinary fair crude glycerol containing 15 per cent residue and 80 per cent glycerol, there would be between 4.5 and 5 per cent of the total glycerol in the foots.

It is considered good practice in distilling all crudes from which the foots can be reworked to give the foots a thorough treatment so that it is not necessary to pay special attention to the percentage of glycerol in the foots. It is easier to clean the still if the distillation is not carried too far, and the capacity of the still is increased. Of course, an exorbitant amount of glycerol is not left in the foots in any case. The aim is to have the residue of 160° C. on the crude carry 40 per cent of its weight of glycerol, in which case the ordinary crude would leave 6 lbs. of glycerol in the foots per 100 lbs. of crude, or between 7 and 8 per cent total glycerol present.

Average practice will obtain 90 per cent of the total glycerol in the crude in the distillate that is ready for boiling down to dynamite glycerol.

The following figures show the distribution of glycerol recovered on a typical dynamite glycerol plant test. These figures are fairly accurate, although not exactly so, as some weights are calculated from measurement. However, they illustrate our purpose:

Sweetwater in evaporator, lbs. ....	1000	
Glycerol by sp. gr., per cent. ....	32.07	
Glycerol, lbs. ....		320.7
Sweetwater in receiver, lbs. ....	1900	
Glycerol by sp. gr., per cent. ....	3.00	
Glycerol, lbs. ....		57.0
Foots, lbs. ....	3600	
Glycerol by analysis, per cent. ....	13.26	
Glycerol, lbs. ....		477.36
Glycerol in concentrator, lbs. ....	17885	
Glycerol by analysis, per cent. ....	99.29	
Glycerol, lbs. ....		17,758
Crude glycerol fed, lbs. ....	23900	
Glycerol by analysis, per cent. ....	79.4	
Glycerol, lbs. ....		18,976

#### SUMMARY

Glycerol in crude, lbs. ....	18,976
Glycerol recovered in sweetwater, lbs. ....	378
Glycerol recovered in foots, lbs. ....	477
Glycerol in dynamite, lbs. ....	17,758
<b>TOTAL RECOVERY. ....</b>	<b>18,613</b>

#### SUMMARY OF PER CENT YIELDS

Dynamite glycerol. ....	94.1
Sweetwater. ....	1.9
Foots (by difference). ....	4.0

The advantages of the distilling system described over older types will be apparent to those familiar with past methods. For the benefit of those not familiar with developments in this field, it may be stated that it was formerly the practice to distil the glycerol, using expanded and reheated steam. The source of supply for the open injected steam was a boiler outside of the glycerol distilling system, so that there was a continuous accumulation of sweetwater which had to be re-evaporated in order to recover its glycerol content. The vapors resulting from this evaporation were not utilized in distilling glycerol but were condensed and run to the sewer. It will thus be seen that the amount of sweetwater which was concentrated under the older systems was much greater than is now required, in fact, the amount of sweetwater concentrated in a modern plant consists only of the fresh water charged to the sweetwater evaporator when starting up the plant plus the water present in the original crude glycerol.