

in platinum crucibles to constant weight). The CaO was determined by the gravimetric method in each sample, there was no silica present and no more than a trace of iron, with these results:

	CaO present by gravimetric method. Per cent.	Calcium oxid found by the oxalic acid method. Per cent.
Sample No. 1.....	57.6	57.6
Sample No. 2.....	50.4	51.0

This indicates that the magnesia does not interfere. Its presence and approximate amount can be judged by the behavior of the titration and quite accurately by continuing the titration if one can spare the time needed.

Iron oxid is sometimes present in impure limes in considerable amount and it obscures or masks the color of the indicator, but if the precipitate be allowed to subside the titration may be carried out to within 1 per cent. of the correct result.

If it is desirable to determine the amount of carbonate present in an imperfectly burned lime it may be carried on as follows:

After grinding the sample to pass 200 mesh weigh out 650 mg. and make the titration in the usual manner; call this result 1-available calcium oxid.

Now ignite some of the finely ground sample in a muffle or over a blast and make another determination, using 650 mg., calling this result No. 2.

Subtract 1 from 2 and divide by 1.78.

Method of Procedure.—The sample must be ground to pass through a 200-mesh screen. Into a 300 cc. Erlenmeyer flask place 50 cc. of distilled water, then add the 650 mg. of the finely ground sample, stopper the flask and shake vigorously for 10 seconds, add two drops of solution of phenolphthalein and then run in the standard solution of oxalic acid until the pink color is discharged, then place in the stopper and shake again.

When the color returns, if it is lime, it will be a bright vivid pink, and the addition of perhaps one-half cc. will be necessary to discharge this color, but if the flask is again shaken and the color returns slowly and is a faint, weak pink this is the end point for the lime.

At all time during the running in of the oxalic acid solution the flask should be shaken as violently as possible, care being taken not to allow it to splash out, so that calcium oxid will pass into solution. In nearly every instance of titrating a high-grade lime the pink color remained vivid nearly to the finish, which shows that the CaO is rapidly soluble. If a completed titration is allowed to stand for from 15 minutes to half an hour the pink color will return and show as brightly as in the beginning.

The reading of the burette is in per cent. of calcium oxid. The solutions necessary are:

Oxalic acid, 14.6068 grams of pure crystals dissolved in enough water to make a liter.

Phenolphthalein 0.5 gram dissolved in a mixture of 50 cc. alcohol and 50 cc. water.

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[CONTRIBUTION NO. 10 FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

DIFFERENTIAL CONDENSATION IN DISTILLATION AND RECTIFICATION OF BINARY LIQUID MIXTURES.

By ALCAN HIRSCH.

The object of this paper is to show the important part which condensation plays in distillation and rectification of binary liquid mixtures, and how the efficiency of operation of commercial plants may be increased by proper partial condensation, especially in the case of alcohol-water. The design of total condensers is well understood, and standard textbooks such as *Verdampfen Kondensieren und Kühlen*, by E. Hausbrand, contain sufficient data on cooling surfaces, radiation, heat transfers, etc., for their correct design and construction. But these same methods of design are usually employed in the case of partial condensers—in fact in commercial practice the same piece of apparatus is often used interchangeably as a partial or total condenser simply by regulating the flow of cooling water. It will be shown that in the case of the design of partial condensers several additional factors enter which have not heretofore been taken into account, and that in the great majority of cases the yield obtained from commercial apparatus, both partial condensers and rectifying columns, may be materially increased by proper condensation without increasing the coal consumption under the boilers.

If a mixture of two miscible liquids of different boiling points be boiled, the composition of the boiling liquid being kept constant, the vapor evolved will be richer in the more volatile constituent than the liquid, unless the latter be of the constant boiling composition, in which case the vapor is of the same composition as the liquid. The curves showing the composition of the liquid and the composition of the vapor in equilibrium with this liquid have been determined for many different mixtures, but for water-ethyl alcohol mixtures with which the experimental part of this paper is concerned, there are three (3) principal curves, as shown in Fig. 1; the Grönig, the Rachewsky, and the Sorel. The Grönig is the original data, but Sorel¹ claims that the composition of the vapor in the upper part of Grönig's curve is greater than the true value, due to partial condensation of the vapor in the upper part of the distilling flask, and Sorel has accordingly applied

¹ *Compt. rend.*, 116, 693.

a correction to the Grönig data. The Rachewsky data seems to be a compromise between the Grönig and the Sorel. E. Hausbrand¹ states that the Sorel data is the most reliable, and that the condensation in practice, where there is always more or less priming, would be much closer to the Sorel curve than the Grönig. The Sorel data were used for all computations in this article where compositions of vapor-liquid are involved, for while they are not absolutely correct, yet they are the best at hand. It is desirable that the equilibrium liquid-vapor composition be known exactly² and that the necessary correction for priming be made for commercial cases.

In order that a vapor may be enriched in respect to the more volatile component, two general methods

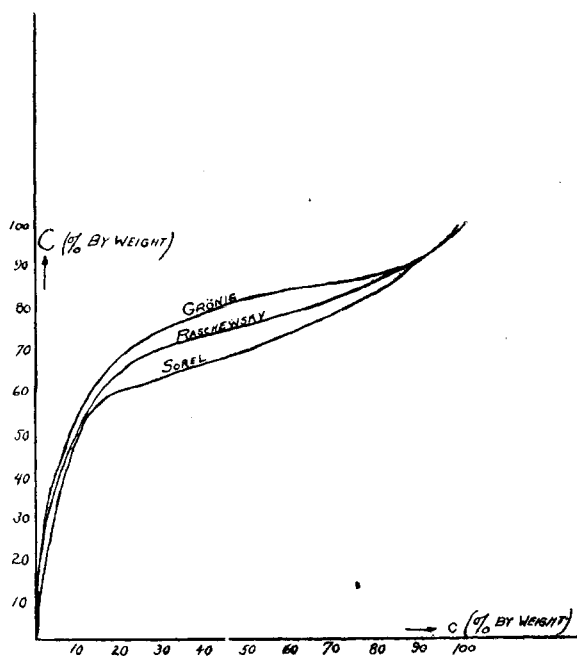


Fig. 1.

of procedure have long been in use. First, there may be induced a partial condensation in which a large portion of less volatile component and a smaller portion of the more volatile component may be deposited in liquid form, depending upon the removal of the latent heat by an external cooling medium, for example running water in a cooling coil. Second, the vapor may be enriched in respect to the more volatile constituent by rectification. This operation consists of an exchange of heat between vapor and liquid mixture only, the condensed vapor delivering its latent heat to the liquid, from which is vaporized in time a new vapor richer in the more volatile component. In order that the last operation may be

¹ E. Hausbrand, *Zeit. f. Chem. Apparut.*, 2, 585 (1907).

² A method for calculating exactly the composition of equilibrium vapor-liquid from thermodynamic data and from some of the laws of physical chemistry has been devised to check Sorel's curve. The results of this work will be presented in a later paper.

continuous each plate must have an appropriate intake and overflow of liquid from the plate above and to the plate below, respectively, the top plate being fed with the condensate from a partial or total condenser.

The nomenclature used in this article is as follows:

The composition of both vapor and liquid is expressed in per cent. by weight of the more volatile component—in the case of alcohol-water, by per cent. alcohol by weight. The composition of the vapor is expressed by C , with subscripts to denote the composition of different vapors such as C_1 , C_2 , etc. The composition of the liquid is expressed by c , with subscripts to denote the composition of different liquids, such as c_1 , c_2 , etc. Furthermore, the compositions of equilibrium vapor and liquid are denoted by the same subscripts, as C_1 , c_1 ; C_2 , c_2 ; the values to be found from Sorel's curve for each specific case. For weight of vapor two letters are used: G with proper subscripts such as G_1 and G_2 for the theoretical discussion, and W with proper subscripts, such as W_1 and W_2 , for actual experimental determinations. For instance, suppose that we wish to enrich a vapor of composition C_1 to a vapor of composition C_2 by partial condensation. By actual experiment a partial condensation is effected, and from a weight W_1 of a vapor of composition C_1 we have remaining a weight W_2 of a vapor of composition C_2 . The ratio W_2/W_1 is called the yield. We can compute by use of the equations shown below the theoretical maximum yield that can be obtained in any given case. A weight G_1 of vapor of composition C_1 will give theoretically a maximum weight G_2 of vapor of composition C_2 . G_2/G_1 is the theoretically maximum yield. Then W_2/W_1 , the actual yield divided by G_2/G_1 , the theoretical yield gives W_2G_1/W_1G_2 , which, multiplied by 100, gives the percentage efficiency.

Since the total heat contained in the weight G_1 of the vapor of composition C_1 remains the same, however, the quantity G_2 of the composition C_2 varies, the percentage efficiency which here represents weight of product may be also taken as the thermal efficiency.

In a paper by Dr. W. K. Lewis,¹ of this laboratory, on "The Theory of Fractional Distillation," it was shown mathematically that the largest possible yield in enriching a vapor from a composition C_1 to a composition C_2 by partial condensation can be obtained when the conditions of a certain differential equation² are fulfilled, and such a condensation was accordingly

¹ THIS JOURNAL, 1, No. 8, 1909.

² If a weight G of vapor of composition C enter a partial condenser; and a weight dG is condensed, then,

$$C.G. = (G-dG)(C-dC) + c.dG$$

$$C.G. = C.G. - G.dC - C.dG + dGdC + c.dG$$

$$dG(C-c) = -G.dC$$

$$dG/G = -dC/C-c$$

$$\ln G_2/G_1 = - \int_{C_1}^{C_2} \frac{dC}{C-c}$$

called a *differential* one. It was also shown that a differential condensation may be considered an infinite series of infinitesimal simple condensations, and is more efficient than a finite series of simple condensations between the same limits of composi-

tion change. The maximum theoretical yield may be computed for any given case graphically from the $(C, 1/C-c)$ curve shown in Fig. 2, by planimentering the area under the curve between the limits of composition change, equating the value to the logarithmic

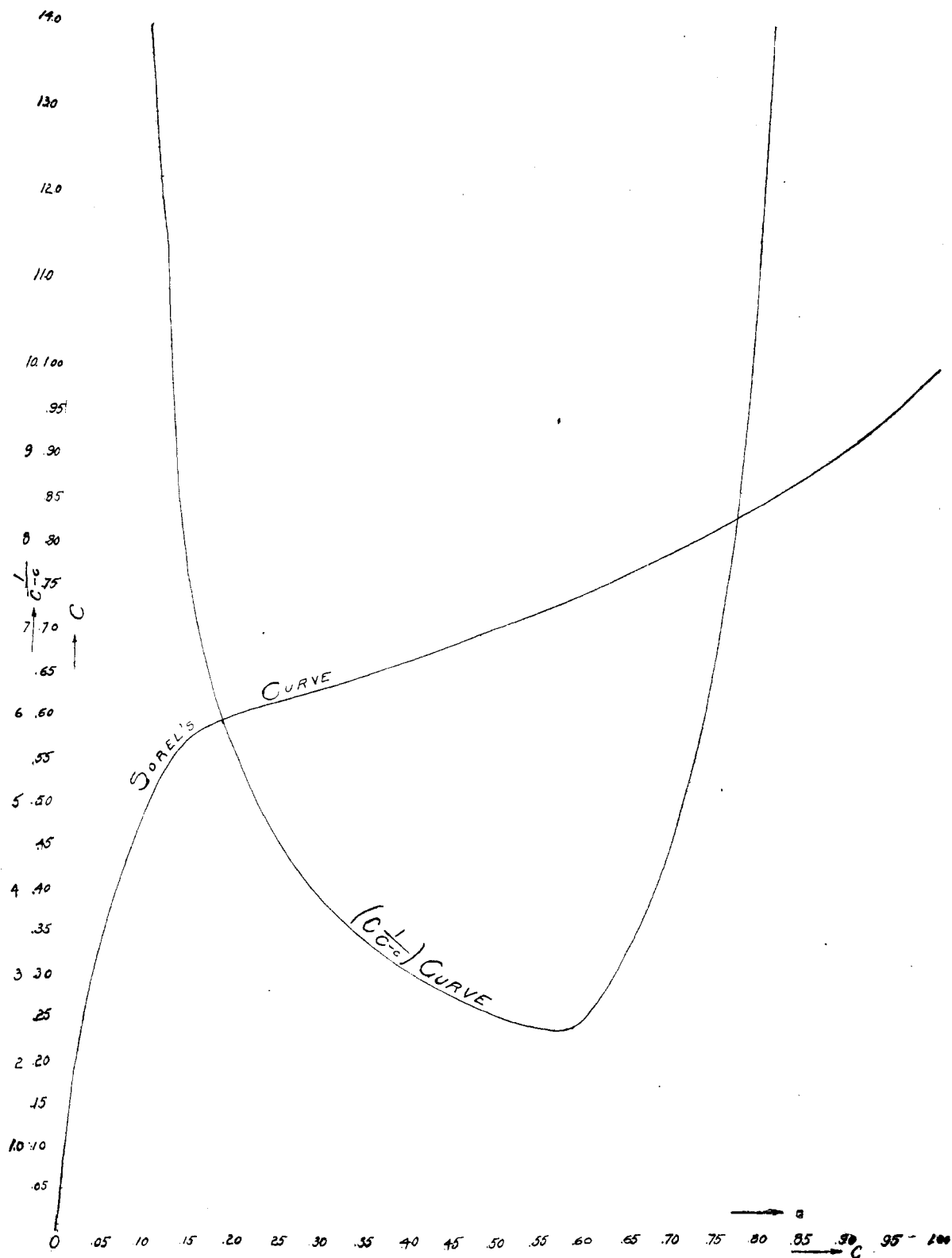


Fig. 2.

equation, and solving. The curves of maximum theoretical yield have been thus computed and are plotted in Fig. 10, so that by reference to these curves the maximum yield may be read off for any given practical case of composition change.

The two extremes of partial condensation are a simple condensation and a differential one, the former being the least efficient and the latter the most efficient. In the case of the enrichment of a vapor by simple condensation, the entering vapor (composition C_1) is condensed to the extent that the condensate (composition c_2) is in equilibrium with the final vapor (composition C_2).

For example, suppose we wish to enrich a 35 per cent. vapor to one of 64 per cent. by one simple condensation, allowing the vapor to come to equilibrium with the resultant condensate. From Sorel's curve we find that the equilibrium liquid of a 64 per cent. vapor has a composition of 31.5 per cent. Assuming that we deal with 100 lbs. of entering vapor, then, 35 per cent. $100 = 64$ per cent. $X + 31.5$ per cent. $(100 - X)$.

$$X = 10.8 \text{ per cent.} = \text{yield.}$$

On the other hand, from an inspection of Fig. 10, showing the maximum yield theoretically obtainable by differential condensation, we find that in the enrichment of a vapor from 35 per cent. to 64 per cent. composition, the maximum yield is 45 per cent. These numerical examples show very clearly to how great an extent the yield depends upon the kind of condensation.

It was desirable first to determine experimentally how closely the differential or maximum yield could be approached. The efficiency obtained would thus indicate how near the actual partial condensation

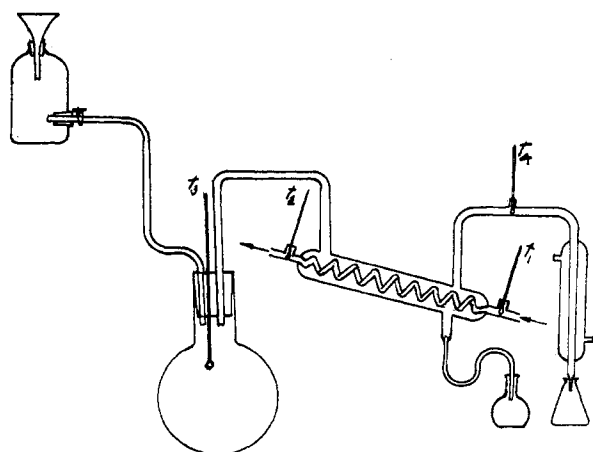


Fig. 3.

was to the desired differential one. From the equations and the nature of the case, in building the first differential condenser the following conditions were fulfilled as nearly as possible:

(1) The vapor should be uniformly condensed, a

very small amount at a time, and the process should be continuous.

(2) The condensate should be removed as fast as formed.

By fulfilling these conditions, there should be a number of very small simple condensations, and the yield of such a series should be much larger than in the case of a single simple condensation. When each

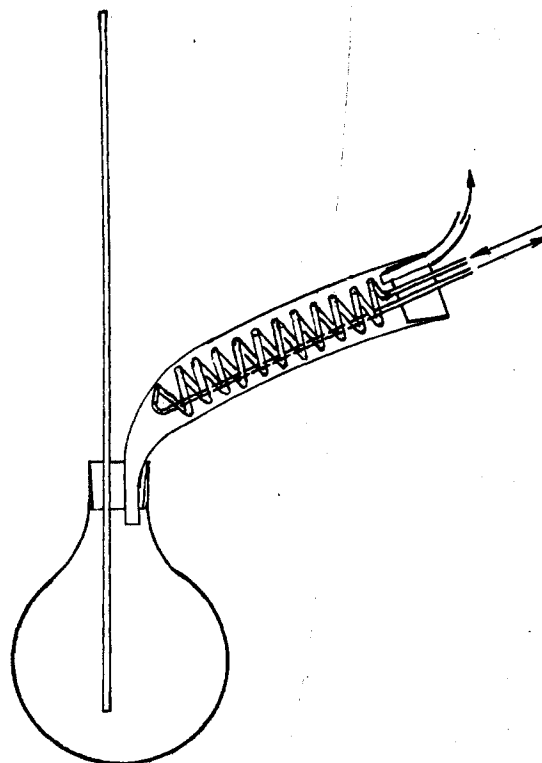


Fig. 4.

small amount of condensate has been deposited it is removed from the sphere of action for if it were allowed to remain, additional and undesired condensation would occur. Each small quantity of condensate should have a correspondingly small quantity of equilibrium vapor, but the condensate as a whole should not be in equilibrium with the uncondensed vapor; in fact the success with which this is prevented determines the efficiency of the partial condensation.

The first apparatus used is shown in Fig. 3. It consisted of a 5-liter R. B. flask and was heated in an oil bath which could be kept constant at any desired temperature. The condenser was of glass with a close-wound spiral through which the cooling water was circulated, the vapors passing around the spiral. The condensate was constantly siphoned off through a goose-neck. The uncondensed vapors from the partial condenser were passed into a total condenser which delivered the final product. The partial condenser, conducting tubes from the distilling flask and to the total condenser, the upper part of the distilling flask and the projecting ends of the spiral, were

all thoroughly lagged with asbestos-magnesia insulating material. No recorded run was made before the apparatus was well warmed up, so that there was no appreciable condensation due to heat conduction from without during a run. The composition of the boiling liquid could be kept approximately constant by a return-feed of alcohol-water mixture. During a run the time was recorded in order to ascertain the rate at which the vapor was passed through the condenser. The samples were collected in tared flasks, the higher alcohol always in an Erlenmeyer, and the watery product in a F. B. flask. The increase in weight of the Erlenmeyer flask is W_2 (composition C_2), and the increase in weight of the F. B. flask added to W_2 gives W_1 , the weight of the entering vapor (composition C_1). The samples were analyzed by determining the specific gravity at constant temperature with a calibrated Westphal plumbet with self-contained thermometer, a chemical balance sensitive to 1/10 mg. being used as the balancing medium. The composition determinations could be checked closely, and this method was found to be entirely satisfactory both as to speed and accuracy.

TABLE I.

Number of run.	t_1 .	t_2 .	t_3 .	t_4 .	C_1 in per cent.	C_2 in per cent.	Rate of vapor.	Eff.
29 B.....	59.0	76.5	92.0	80.0+	49.5	74.5	13.2	17.7
30 B.....	59.0	76.5	92.5	81.0	48.2	69.3	16.9	47.5
31 B.....	59.0	77.0	92.3	85.0	48.1	68.7	21.5	77.8
32 B.....	59.0	77.5	92.5	85.5	46.8	67.3	22.5	77.4
33 B.....	59.0	78.0	92.5	86.5	45.0	63.8	24.6	83.5
34 B.....	59.0	76.0	92.5	86.0	42.9	63.7	24.1	84.5
35 B.....	59.0	76.0	92.0	85.0	47.1	66.4	24.8	84.8
36 B.....	59.0	76.5	92.0	86.0	45.3	63.6	27.5	88.9
37 B.....	59.0	76.0	93.0	82.8	41.7	67.9	14.5	33.8
38 B.....	59.0	76.5	93.0	84.0	41.0	64.3	15.8	40.6
39 B.....	59.0	76.0+92.0		85.6	48.4	66.6	28.0	90.8
40 B.....	59.0	76.5	93.0	87.5	46.9	61.8	37.8	95.0
41 B.....	59.0	83.0	92.5	85.0	43.4	66.8	22.7	77.5
42 B.....	59.0	85.0	92.5	85.5	46.0	66.1	24.8	91.4
43 B.....	59.0	85.0	92.0	85.5	47.4	65.5	29.5	92.2
25 A.....	52.0	69.0	91.5	82.0	49.0	71.5	21.4	35.0-
8 A.....	57.0	79.0	96.0	85.0+	25.0	65.5	12.9	50.0-
10 A.....	64.0	84.0	94.0+	89.0	39.4	57.3	15.0	87.0
11 A.....	59.5	84.0	94.0	89.0	36.4	58.5	13.8	71.6
22 A.....	59.0	77.0	92.5	85.0	47.0	65.5	26.4	87.0

t_1 = temp. of entering cooling water.

t_2 = " " exit " "

t_3 = " " entering vapor.

t_4 = " " exit vapor.

Besides the preliminary series to determine the best method of manipulation, forty-three runs were made with the small apparatus and a number of these results are presented in Table I. An inspection of this table will show that in enriching a vapor from a low to a higher alcohol content the enrichment may be done with either a low or a high efficiency. A closer study will reveal that the efficiency depends upon the following factors: The rate of the passage of vapor must not be too low or otherwise a continuous and steady operation is impossible, and instead of differential there is apt to be only simple condensation in a portion of the apparatus. In the small laboratory apparatus used the minimum rate

for satisfactory operation proved to be about 25 cc./min. The temperatures of both the entering and the leaving cooling water is perhaps the most important factor in differential condensation. Suppose that a vapor entered the differential condenser at a temperature of 92° C. If the condensing surface at this end of the condenser is at a considerably lower temperature (say 20° less) it is easy to see that there will be a large condensation of vapor at this point. Not only must there be no material "jump" in temperature between the cooling surface and the entering vapor, but the same conditions must hold for the exit vapor and its cooling surface. In fact throughout the condenser, for an efficient condensation, the change in temperature of the vapor from its entrance to its exit must be uniform—theoretically it should be differential from point to point. The heat conductivity of glass being so small, the temperature on the outside of the glass spiral is considerably higher than the temperature of the cooling water at that point, and for this reason a metallic spiral should be used. Silver would be preferable, but copper or even tin serves this purpose very well.

An apparatus for laboratory use for the separation of miscible liquids by fractional distillation is sketched in Fig. 4. The condenser, which can be very easily and quickly, as well as cheaply, made, consists of an adapter tube with a small copper coil placed within. The copper return is covered with a glass tube to prevent condensation except along the surface of the spiral. The ordinary laboratory still-head, such as the Hempel, rod-and-disc, evaporator, etc., are fragile and expensive, and the enrichment of the vapor depends entirely upon condensation by air conduction (in some cases there is a very slight enrichment due to rectification). On account of the poor conductivity of glass the capacity is exceedingly small, the ordinary delivery of final condensate being about one drop per second. By using an adapter tube with copper spiral and regulating the temperature and rate of the entering cooling water to the proper values as explained above, 25 cc./min. or more of final distillate may be obtained with equally efficient separation.

The results with the small glass apparatus were so encouraging that it was decided to build a larger differential condenser and to try the idea on as large a scale as could be conveniently handled in this laboratory. The diagram of this differential condenser is shown in Fig. 5. The condenser consisted of a



Fig. 5.

galvanized iron pipe, 3" inside diameter and 4 ft. long, with reducing caps, 3"-1", at the ends. The spiral

consisted of 20 feet of copper tubing 1/4" o. d. No. 20 gauge, wound to fit inside the galvanized pipe. The condenser and all communicating tubes and pipes were heavily lagged with steam pipe insulation. In the first experiments the cooling water was circulated by gravity with a head of about 8 1/2 feet, the water being heated by live steam in an elevated barrel of thirty gallons capacity. Even with suction the circulation was not as fast as was desired in some experiments, and so an iron tank of 60 gallons capacity was used as a reservoir, in which the water was heated by steam to the correct temperature, and by means of compressed air was circulated at the desired rate. In the later experiments an electrically driven gear pump was used and proved very satisfactory. A comparatively small amount of water could be used over and over, and the temperature was regulated simply by slightly cooling the exit water by radiation. By inserting resistance in the armature circuit of the motor, any desired rate could be had and maintained constant.

The still for supplying the vapors was of copper, 20 liter capacity with the bottom steam-jacketed. The still and entire steam system from calorimeter to exhaust was thoroughly insulated. However, when steam was used as a heating medium it was found impossible to maintain a constant rate of vapor even with a needle-valve adjustment and direct atmospheric exhaust, owing to the low quality of the steam and variations in the line pressure.

Electrical heating was finally resorted to and proved entirely satisfactory. An inexpensive heater of simple construction, which gave excellent service, consisted of ten arc-carbons, one-fourth inch diameter and about eleven inches long, mounted in two wooden rings (preferably white pine or cypress) o. d. 7 1/2", i. d. 4". The carbons were connected in series by cast lead lugs, and the bottom was of wood which insulated the heater from the still, and was weighted with lead to keep it firmly seated. 25 amp. at 100 V. through this heater delivered over 75 cc./min. from 15 liters of a low alcohol.

With the single coil differential condenser 76 recorded runs were made and a number of different series are presented in Tables II and III. The amount of cooling water used was not measured in many of the early experiments, owing to the difficulty of accurately measuring it with the circulation system used at that time (gravity and suction). But in later experiments this was done and is discussed in detail further on.

Curves A and B shows the influence of temperature of the entering cooling water on the results obtained, and emphasize the effect of this temperature on the efficiency.

The great importance of having the temperature of the entering cooling water high enough was shown

TABLE II.

Number of run.	t_1 .	t_2 .	t_3 .	t_4 .	C_1 .	C_2 .	Rate ¹ of vapor.	Eff.
10 C.....	63.0	89.0	93.0	88.5	53.4	62.4	92.0	73.7
12 C.....	60.0	91.0	93.0	88.0	47.1	60.0	114.5	51.8
13 C.....	55.0	90.0	93.0-	90.0+	41.8	51.0	200.0	65.4
14 C.....	72.5	90.0	94.0	90.5	39.5	52.0	90.0	74.5
15 C.....	58.0	90.0	94.0+	89.0	38.0	58.0	86.5	26.0
16 C.....	59.5	91.5	95.0+	88.5	37.0	58.0	90.0	13.8
18 C.....	69.0	92.0	95.5	89.5	34.0	50.2	46.0	50.7
19 C.....	61.0	91.5	95.5	91.5	34.0	49.0	77.5	46.0
20 C.....	74.0	90.0	95.0	86.0	36.8	66.8	50.0	73.3
21 C.....	76.0	91.0	95.0	90.0-	32.7	55.4	55.4	79.5
22 C.....	74.0	93.0	95.5	90.0+	33.0	51.0	55.7	52.0
23 C.....	75.0	91.5	95.5	89.5	30.7	55.4	53.0	75.5
24 C.....	75.0	92.0	95.5	90.0+	30.6	44.0	75.0	75.0
25 C.....	72.0	90.5	94.5	90.0	36.4	56.0	70.8	65.6
26 C.....	78.5	91.0	94.5	89.5	36.1	56.4	62.9	82.0
27 C.....	77.0	90.0	94.0	90.0	40.5	55.7	68.9	89.0
28 C.....	78.5	90.0	94.0+	89.5+	39.9	56.4	53.2	91.0
29 C.....	81.0	90.5	94.5	89.0	36.4	56.4	53.5	88.0
30 C.....	78.5	90.5	94.0+	89.0+	35.0	57.7	52.0	82.8
31 C.....	78.5	90.5	94.0-	90.0+	36.7	47.5	77.0	81.5
32 C.....	79.0	89.5	93.5	89.0	40.0	59.2	69.0	82.0
33 C.....	80.0	88.0	93.5	86.0	41.9	67.0	41.4	83.6
34 C.....	78.5	88.0	93.5	87.5	39.6	64.8	36.2	85.4
35 C.....	78.0-	89.0	93.5	87.5	41.7	62.8	57.8	71.0
36 C.....	80.0	90.5	94.0+	91.5	36.3	49.7	69.8	90.0
37 C.....	82.0	90.0-	94.0+	89.0-	37.9	60.5	35.6	85.5
38 C.....	79.5	90.5	94.0+	91.0	37.6	50.4	48.7	86.1
39 C.....	80.0	90.0	94.0-	87.5	38.7	64.0	40.6	82.7
40 C.....	78.5	90.5	94.0+	90.0+	36.1	53.4	59.4	81.7
41 C.....	78.5	90.5	94.0+	90.0+	34.9	56.3	35.8	79.0
42 C.....	80.5	90.0	94.0-	90.5	38.1	54.2	67.0	82.7
43 C.....	81.0	90.0	94.0+	90.5	36.5	54.7	40.4	81.6
44 C.....	81.5	84.5	89.0-	83.5	58.2	74.3	27.8	100.0
45 C.....	81.0	84.0	89.0	84.0-	57.3	73.9	32.5	100.0
46 C.....	79.0	86.0	94.0	82.0+	37.5	73.4	61.5	86.0
49 C.....	80.8	86.0	93.0	84.0-	45.5	70.1	53.5	92.8

TABLE III.

Number of run.	t_1 .	t_2 .	t_3 .	t_4 .	C_1 .	C_2 .	Rate ² of vapor.	C. W.	Eff.
1 E....	74.5	79.0	81.3	79.0	76.0	83.3	50.6	2125	73.6
2 E....	76.3	78.3	81.8	78.5	76.6	83.5	32.7	2000	57.7
3 E....	76.4	78.4	81.5	78.0	75.7	83.6	24.4	1600	58.8
4 E....	76.6	78.1	81.9	78.0	75.2	83.3	23.5	2280	37.1
5 E....	75.6	79.0	81.5	79.2	76.8	81.4	32.4	1350	73.8
6 E....	76.0	78.0	81.9	78.0	75.6	85.6	18.1	1275	57.0
7 E....	76.5	78.1	82.0	78.0	77.0	84.5	19.7	1206	81.9
8 E....	75.0	78.3	82.3	77.3	75.7	81.7	19.7	1000	38.9
9 E....	75.0	78.6	82.8	78.0	73.7	84.2	46.6	2740	45.5
10 E....	77.8	78.0-	82.0	78.0+	79.0	85.8	23.4	3000	100.0
11 E....	77.6	78.0	82.2	78.9	76.4	82.8	20.0	2980	62.2
12 E....	77.8	78.0	81.8	79.0	77.3	83.4	17.0	2740	81.4
13 E....	78.0	79.0	80.0	...	78.8	83.4	15.1	1830	87.6
14 E....	77.5	78.0	81.4	78.0	71.7	82.5	15.2	2680	96.7
15 E....	77.5	78.0	82.0	78.5	76.1	83.7	17.8	2625	100.0
16 E....	77.5	78.0	82.0	79.0	76.5	82.8	17.5	2325	95.4
17 E....	77.5	77.5	81.2	77.5	79.2	84.3	16.6	2675	90.0
18 E....	77.5	77.5	81.2	78.5	79.4	83.3	19.2	2480	89.2
19 E....	77.5	77.5	81.1	77.5	80.4	85.5	15.1	2200	65.0
20 E....	77.9	78.0	81.0	78.5	80.0	84.4	12.6	2370	100.0
21 E....	77.5	77.5	81.2	78.0	79.9	84.2	13.2	2525	90.8
22 E....	77.0	77.0	80.3	78.0	79.9	84.3	10.5	2425	78.0
23 E....	77.1	77.1	80.1	77.0	80.6	84.4	10.0	2375	85.6
24 E....	76.9	77.0	80.2	78.0	79.6	84.3	10.5	2640	68.0
25 E....	76.6	77.0	80.2	77.5	80.8	85.1	12.6	2725	70.0
26 E....	76.4	77.0	80.1	76.5	80.0	85.6	10.9	1100	50.5
27 E....	76.6	77.0-	79.9	77.8	81.8	85.5	19.2	1130	96.6
28 E....	76.7	77.0	80.0	77.6	82.0	85.9	23.0	2630	100.0
29 E....	76.5	77.0	79.8	75.0	81.2	85.6	15.0	1540	56.2
30 E....	76.5	77.0	80.0	78.0	83.0	86.0	22.2	1260	100.0
31 E....	76.5	77.0	80.0	78.0	80.9	86.3	20.5	1720	86.0
32 E....	76.5	77.0	79.9	78.0	82.4	85.9	26.1	1175	48.5
33 E....	76.5	77.5	80.1	78.0	81.9	85.9	23.1	1816	90.8
34 E....	76.5	77.5	80.1	78.0	81.7	85.8	26.8	1725	98.5
35 E....	76.0	77.0	80.1	76.7	80.9	89.1	18.3	1566	67.0
36 E....	76.0	77.5	80.2	78.5	81.5	85.9	21.6	1320	83.1
37 E....	76.0	77.5	80.3	78.0	81.8	85.4	21.4	1018	95.8

¹ Rate of vapor in cc. per minute.

² Rate of vapors and cooling water given in grams per minute.

recently by a case in commercial practice where cold water had previously been used in a partial condenser. When the temperature of the entering cooling water was raised and the amount properly regulated, the yield was double the best that had heretofore been obtained using cold water, and yet the enrichment of the vapors was the same in both cases.

The area of the cooling surface of the coil in the differential condenser was not as large as was desired, and it was feared that some of the vapors could probably pass through the space inside the coil at a high velocity without being properly enriched. Moreover, when the rate of vapor passage was rapid the air pressure required to supply the cooling water was so high that the rate of water circulation could not be kept constant. For these reasons a double coil was substituted for the single coil and was built as follows: A copper coil of the same length, diameter, and gauge as the original one was wound to fit within the first coil and the two coils were brazed together at each end. The second coil was wound left-handed with respect to the first, in order to hold it rigidly in place. The cooling water had two parallel paths of equal resistance to traverse, and thus with the same pressure heretofore used, twice the amount of water could be circulated. Baffle plates were placed within the inner coil to insure a thorough mixing up of vapors, and to prevent any vapor passing through the center of the condenser. The results obtained with this differential condenser are given in Table IV.:

TABLE IV.

Number of run.	t_1 .	t_2 .	t_3 .	t_4 .	C_1 .	C_2 .	Rate ¹ of vapor.	Eff
1 F.....	77.3	81.5	88.0	81.3	57.4	77.2	58.5	100
2 F.....	78.5	81.5	88.0	81.8	57.7	75.9	55.0	100
3 F.....	79.2	82.3	88.5	82.5	58.3	74.4	52.9	100
4 F.....	79.0	83.0	91.5	81.0	47.5	77.9	34.4	100

The proper amount of cooling water to use in any differential condensation was determined in the following manner:

Suppose that a weight of vapor W_1 , composition C_1 , enters the differential condenser, is partially condensed, the uncondensed vapor having the weight W_2 , composition C_2 , and the condensate having the weight W_3 , composition c_3 .

We know that

$$W_1 = W_2 + W_3$$

and

$$C_1 W_1 = C_2 W_2 + c_3 W_3.$$

L_1 = total heat in vapor, composition C_1 .

L_2 = total heat in vapor, composition C_2 .

H_3 = heat in liquid, composition c_3 .

K = weight of cooling water.

The total heat must be equal to the sum of its components, and therefore for any case,

$$L_1 W_1 = L_2 W_2 + H_3 W_3 + K(t_2 - t_1).$$

¹ Rate of vapor in grams per minute.

The values for L and H are given in Hausbrand's article.¹ For any specific differential condensation, we have seen that the temperature t_1 and t_2 are fixed, t_2 being slightly below the temperature of the entering vapor and t_1 slightly below that of the exit vapor.

From the thermal equation given above it is seen that a certain definite quantity of heat, $K(t_2 - t_1)$ per unit of time must be removed by the cooling water, and as the temperature change ($t_2 - t_1$) is fixed, the amount of cooling water K must be a certain quantity, and can be calculated for each specific case.

In order to check this method the data from a very efficient run was used, and the calculation made as given below:

Rate = 44.5 grams = 0.098 lb. vapor per minute.

C_1 = 45 per cent.

C_2 = 74 per cent.

Rate cooling water = 5.5 lbs. per min.

$t_2 - t_1 = 9^\circ \text{F.}$

Maximum yield = 40 per cent.

c_3 = 25.7 per cent.

From tables (*l. c.*):

L_1 = 822 B. t. u.

L_2 = 628 B. t. u.

H_3 = 119 B. t. u.

Then,

$$0.098 \times 822 = (0.40 \times 0.098)628 + (0.60 \times 0.098)119 + (5.5 \times 9).$$

$$80.5 \text{ B. t. u.} = 24.6 + 7.0 + 49.5 \text{ B. t. u.} = 81.1$$

In some of the cases given in Table III the thermal equations will not check as closely as in the example given above, but these discrepancies are due to the fact that in series E the temperature differences of entering and exit cooling waters were very small and the temperature could not be read exactly because the thermometers were placed in oil wells. In the numerical example given above the temperature difference was large and therefore the percentage of error in determining $t_2 - t_1$ was small.

In designing and building a differential condenser for commercial use the following method should be followed: The capacity of the condenser is known and the change in temperature of the cooling water is also approximately known for any change of composition of the vapors from C_1 to C_2 . It is known that the heat transfer must be made in a certain manner to obtain the maximum yield. From tables on the heat conductivity of copper the surface is calculated, and allowing for fairly close-coiling, and several coils being placed one within the other, the size of copper tubing to use is determined approximately. The size of tubes should be chosen of sufficient diameter to conduct easily the amount of cooling water necessary (see tables of flow of liquids through tubes). The weight of cooling water can be calculated as

¹ *Loc. cit.*

shown above and if the apparatus is operated properly a high efficiency is assured.

A series of experiments were made to determine if the performance of the differential condenser is as efficient at high condensations as it is at low, and the results of this work are given in Table III. The apparatus is more difficult to regulate at the high concentrations, as each corresponding c and C lie closer together as the constant boiling mixture is approached and consequently the temperatures of the entering and exit cooling water must be delicately adjusted. In some cases a difference of a few tenths of a degree in the temperature of the entering cooling water materially affected the efficiency in that particular run. Fluctuations in temperature, rate of cooling water or vapor that would not be noticed at low concentrations were troublesome at high. An apparatus in which a composition change of 40 per cent.

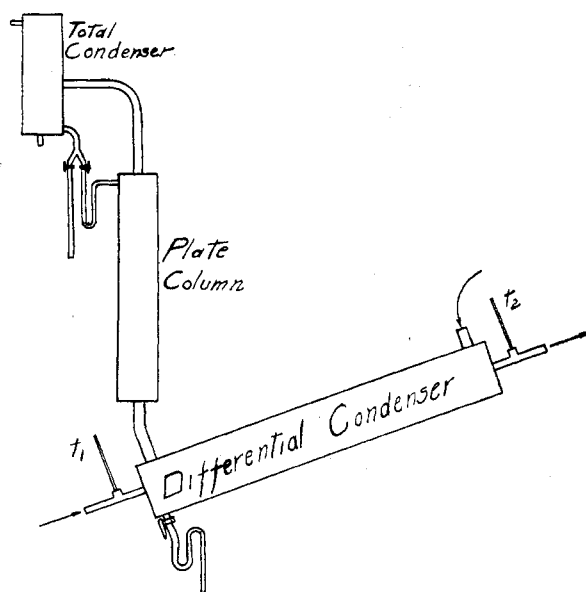


Fig. 6.

can be easily effected at low concentrations may only be large enough to give a composition change of 10 per cent. or less at high concentrations. So if a 190° proof alcohol is desired, the size of the differential condenser may be several times as large as that necessary if only 145° proof alcohol is required, if the passage of the vapor be rapid. Except for the susceptibility of the apparatus to slight changes of temperature and rate, and the increased size of apparatus necessary if the output is large, it is not especially difficult to obtain a high alcohol at a high efficiency by differential condensation. With the single coil apparatus a 186° proof alcohol at approximately 100 per cent. efficiency was obtained.

A differential condenser of medium size (compared with the size of the ordinary dealcoholating and rectifying columns) and large capacity, which will

enrich the vapors from about 25 per cent. to 75 per cent., can be built and run at a high efficiency, but for higher alcohols the differential condenser cannot be so conveniently used for reasons given above. As the high proof of the rectified alcohol is of first importance to many distillers, it was desired to be able to produce as high a proof as was wanted at a high efficiency of operation.

An efficiency test on one of the very latest types of French distilling apparatus was made by the writer, and the thermal efficiency of the rectifying column alone was computed as 40 per cent. of the theoretical maximum, which is high for the average column. The composition of liquid and vapor in different parts of the apparatus was as follows:

Composition of final distillate, 193° (96.5 per cent. by vol.).
 Composition of vapors entering bottom plate, C_0 = 20.6 per cent.
 Composition of vapors entering second plate, C_1 = 58.5 per cent.
 Composition of vapors entering third plate, C_2 = 68.0 per cent.
 Composition of liquid on the bottom plate, c_1 = 14.2 per cent.
 Composition of liquid on the second plate, c_0 = 43.2 per cent.

This test showed that the composition change on the bottom plates was very rapid, and as the change from successive plate to plate is done by simple rectification, the yield in this part of the apparatus was poor. The column tested had eighty-eight plates, of which the greater number were used for rectification of high vapors.

The ordinary type of rectifier column can be more efficiently operated if the apparatus is well insulated and if the composition change from plate to plate is small. Ordinarily, this latter would mean that an apparatus twice the size of the one in use for the same composition change and the same capacity would be required, and on account of cost of installation this is prohibitive. Many designers have tried to build apparatus having large capacity and a small number of plates, and the operation depended upon the rapid enrichment of the vapors in the bottom plate. Although the first cost is reduced, it is impossible to obtain a high efficiency with such an apparatus because the total rectification is a series of simple rectifications of large composition change, and the yield is therefore low. In case it is desired to obtain high proof, the last step in concentration can most successfully be accomplished by using a plate column. Above this a total condenser, returning the calculated amount of overflow from the same to the top plate, will usually be found most satisfactory, requiring much less attention at this high proof and yielding results almost as economical as a differential type. This is due to the fact that the composition of vapor and liquid at these high proofs lie so close together. A differential condenser is not suitable for the last step in concentration for high alcohols but can be most successfully used during the earlier steps of rectification.

Fig. 6 is a sketch of a plate column of eight plates

delivering into a total condenser with return-feed to the top plate, the rectifying column being placed above a differential condenser. The proper return-feed from the total condenser is calculated as follows:

It has been shown¹ that a rectifying column is working at its maximum efficiency when the composition of the overflow from the bottom plate is equal to that of the equilibrium liquid of the vapor entering the bottom plate. If the composition of the entering vapor is C_o , that of the rectified vapor C_c , then for W_o pounds of entering vapor the maximum yield of final product W_c is given by the equation

$$\frac{W_c}{W_o} = \frac{C_o - c_o}{C_c - c_o}$$

The total weight of alcohol mixture of composition C_c that can be obtained from the weight of entering

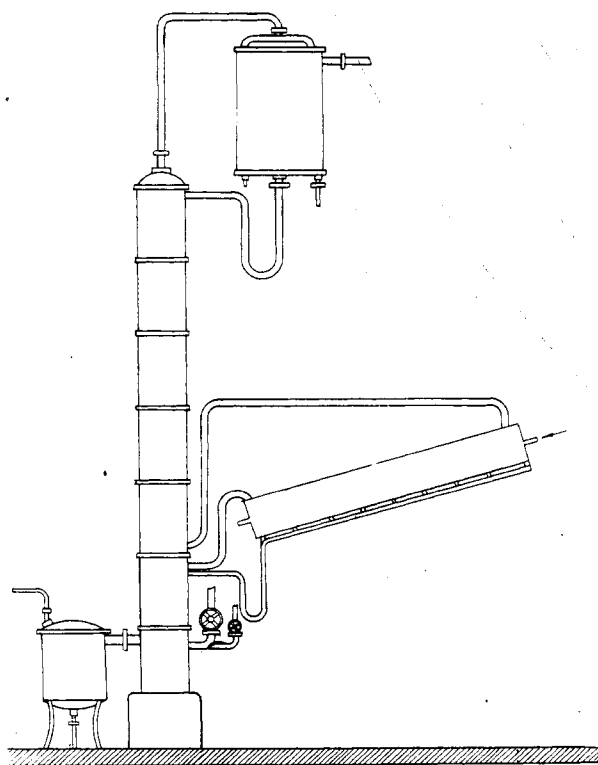


Fig. 7.

vapor W_o , composition C_o is calculated, and after subtracting the maximum yield W_c the remainder gives the amount of distillate of composition C_c that should be returned to the top plate of the plate column.

The results of a test with the apparatus of Fig. 6 are as follows:

Composition of vapors entering diff. cond. = 45.1 per cent.
Rate of vapors entering diff. cond. = 44.5 gram./min.
Composition of vapors leaving diff. cond. = 74.0 per cent.
Composition of final product from plate column = 85.3 per cent. (by vol. 90 per cent.).

The double coil differential condenser was opera-

Lewis, *Loc. cit.*

ted under conditions which previous tests had shown allowed a very high efficiency to be obtained.

Forty and five-tenths per cent. of the vapors condensed in the total condenser were returned to the

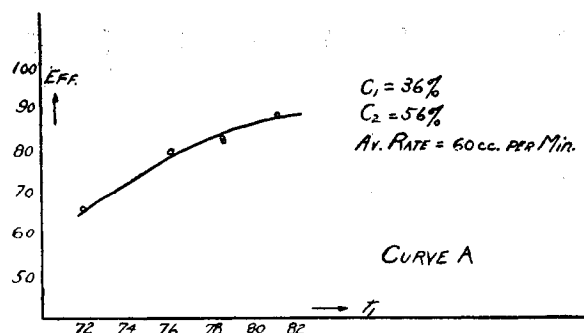


Fig. 8.

top plate. The theoretical amount to be returned for a composition change from 74 per cent. to 85.3 per cent. was 38.8 per cent., calculated from the formula:

$$\text{Max. yield (for plate columns)} = \frac{C_o - c_o}{C_c - c_o}$$

The actual yield of final product was 22.86 grams in $2\frac{1}{2}$ min.; 111.35 grams of 45.1 per cent. vapor entered the condenser, and the maximum yield (40 per cent. of the weight of entering vapor) = 44.56 grams of 74 per cent. vapor entered the plate column, and was enriched to 85.3 per cent. in that space of time ($2\frac{1}{2}$ min.).

The maximum yield of the final product was:

$$W_c = W_o \frac{C_o - c_o}{C_c - c_o} = 44.56 \frac{0.74 - 0.59}{0.853 - 0.59} = 44.56 \times 0.57 = 25.4 \text{ gm.}$$

The yield obtained was 22.86 grams.

$$\text{Efficiency of total operation} = \frac{22.86}{25.7} = 90.2 \text{ per cent.}$$

The apparatus was run in this manner for several consecutive days for about 10 hours daily, and the performance was perfectly steady and constant at all times. The plate column used had only eight plates,

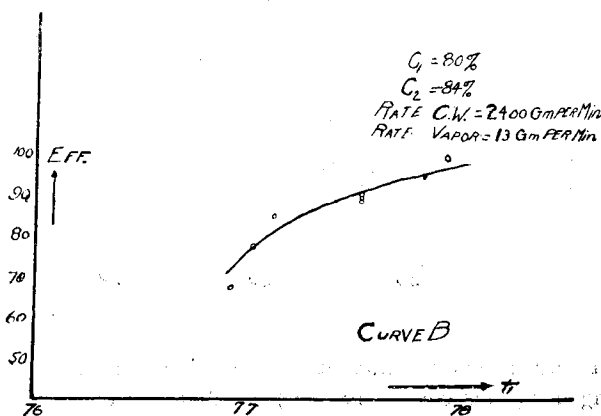


Fig. 9.

but if enough plates are used, and this method carefully followed, an alcohol approaching the composition of the constant boiling mixture can be obtained. The apparatus as run in the above test corresponded

apparatus being 90 per cent. of the theoretical maximum.

It was shown¹ that a differential condenser placed above a plate column and returning the differential

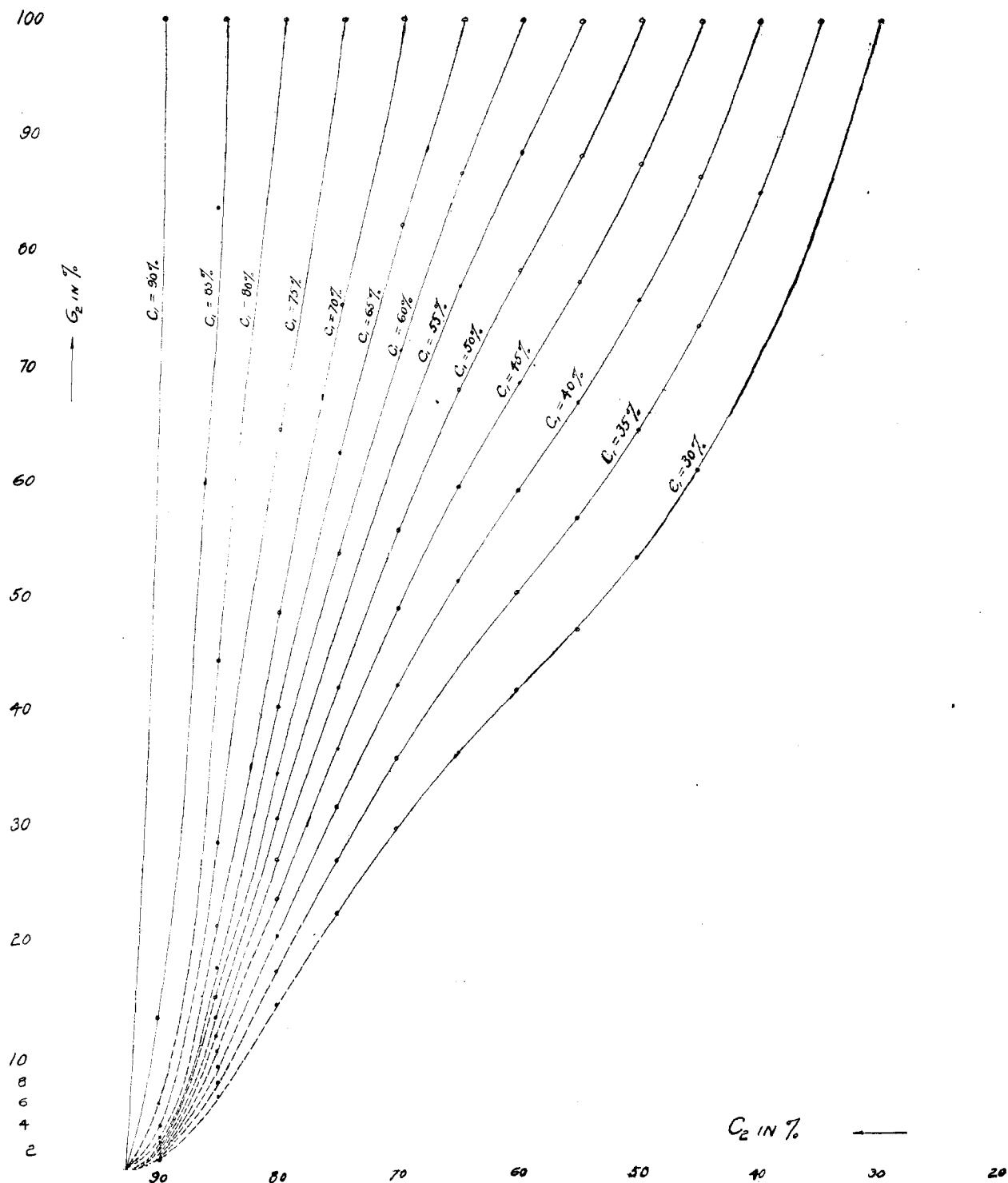


Fig. 10.

to a continuous distillation and rectification apparatus using a 14 per cent. (by vol.) mash and delivering a 90 per cent. (by vol.) alcohol, the performance of the

condensate to the top plate reduces the number of plates necessary to a minimum and enables the

¹ Lewis; *Loc. cit.*

operation of the plate column to be made at a high efficiency. The condensate from a differential condenser should never be returned directly to the still, but should always be passed through a short plate column which removes the maximum amount of the volatile component from the condensate, and the overflow from the bottom plates is of approximately the same composition as the liquid in the still—the condition of maximum efficiency.

Fig. 7 shows the arrangement which should be used to increase the efficiency of commercial rectifying columns. The rectifying column is made into two columns, the lower one being rather short, by placing a solid metal sheet between two successive plates. The lower column should contain fifteen or twenty plates,¹ and the vapors from the top plate of this short column should pass into the differential condenser,² and after being properly enriched (a composition change of 50 or 60 per cent.) should then pass into the upper plate column for rectification for proof. The vapors from the top plate of the upper column should pass into a total condenser and the calculated amount returned to the top plate. The overflow from the bottom plate of the upper column should pass into the top plate of the lower column, and if the whole apparatus is well lagged, a high efficiency is easy of attainment. In case high proof (above 85 per cent. by volume) is not required, the upper column may be omitted.

The differential condenser is simply and cheaply built, the proper design of the coil being most important. The cooling water is used continuously, and some method of initially heating it to the proper temperature, either with live steam or coils, should be used. The circulation may be accomplished by either a force or gear pump, or in some cases gravity flow might give the volume required. The exit cooling water may be cooled down to the proper intake temperature by spray or by flow over baffle plates.

CONCLUSION.

An apparatus has been developed for partial condensation of mixed vapors, to be used in conjunction with a plate rectifying column below it, and if necessary with a further column above it, which will:

(1) Materially increase the thermal efficiency and capacity of commercial types of rectifying apparatus, and

(2) Decrease the initial cost of the same by decreasing the length of the plate towers used.

Extensive experimental results have been submitted to prove the accuracy of the deductions and conclusions, and to furnish data for the proper design

¹ The correct methods of design for such a column can be found in Lewis' article.

² It will be noticed that in Fig. 7 the differential condenser is tipped so that the condensate flows towards the entering vapor. This is for the purpose of preventing any depletion whatever of the vapor in volatile component, although the condensate is removed as fast as formed from the sphere of action by tubes shown in the sketch.

of such apparatus; the methods and calculations for such designs have been outlined.

CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM, AND THE DETECTION OF CAPSICUM.

By E. K. NELSON.

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Thresh,¹ in 1876, established the fact that a crystalline, powerfully pungent principle, which he named capsaicin, is the main active body in capsicum.

Morbitz² isolated a principle from capsicum which he termed "capsacutin," but Micko,³ who has done the most recent work on the subject, showed that the body isolated by Morbitz is identical with the capsaicin of Thresh, being probably an impure form of the latter body.

Micko developed a process for the isolation of capsaicin and proved it to be the pungent principle of pepper (*capsicum fastigiatum*), but that *capsicum fastigiatum* contains about twenty times as much capsaicin as does *capsicum annum*.⁴

In view of the fact that the detection of capsicum is desirable in those cases where it is used to fortify pungent beverages, such as ginger ale, it seemed desirable to isolate some of the pure principle for the purpose of studying some of its properties.

The method of Micko was employed, and while extremely tedious and difficult, it is apparently the only way at present known whereby the body can be satisfactorily separated from the fatty and resinous bodies with which it is associated.

Fifteen hundred grams of ground African cayenne were completely exhausted with ether. The ether was distilled off and the residue, a red, very pungent oil, was dissolved in 1 liter of 90 per cent. alcohol, made slightly alkaline with alcoholic potash, and well agitated. A portion of the oil remained undissolved. This was separated, agitated with 90 per cent. alcohol, and the alcoholic solutions, which contained the pungent principle, were united. Barium chlorid solution was added to the alcoholic solution in moderate excess and the mixture was thoroughly agitated. After standing for several hours, the clear liquid was decanted from the precipitate and the latter was washed with alcohol on a glass wool filter.

The alcohol from the alcoholic solution was removed by distillation, and the residue was agitated with warm water. On standing, an oil separated, which was removed and the aqueous layer was shaken out with chloroform, the residue from which was united with the main portion of oil. The oil was taken up with 90 per cent. alcohol, exactly neutralized with alcoholic potash, and sufficient alcohol added to bring

¹ *Phar. Jour. and Trans.*, **3**, 7, 21, 259, 473.

² *Phar. Zeitsch. f. Russland*, **1897**, 369.

³ *Zeits. f. Unters. d. N. u. Genussm.*, **1898**, 818.

⁴ *Ibid.*, **1899**, 411.