Recovery of beta-pinene from crude sulfate turpentine
by Gene Richard Peters

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
Montana State University

Abstract:
The object of this project was to develop an economical method to obtain high-purity beta-pinene from Waldorf-Hoerner crude sulfate turpentine produced at Missoula, Montana; The basic raw material for this project was the crude sulfate turpentine from the Waldorf-Hoerner mill. The alpha-pinene and delta-3-carene content of the crude varies extensively over any given period of time, but the beta-pinene content,remains quite constant at 10 percent of the crude.

Batch distillation was used as the method of separating the turpentine into pure components. The material most frequently used as a distillation charge, for the project was a fraction of the crude turpentine consisting of 40.0 percent alpha-pinene, 4.5 percent camphene, 24.0 percent beta-pinene, and 31.5 percent delta-3-carene.

Gas chromatography was used for compound identification and determination of sample compositions.

The effects of column height, reflux ratio, and steam on the separation of the turpentine components were, investigated. Scouting experiments showed that a 45 theoretical plate column operating at a 30:1 reflux ratio and steam distillation would have to be employed to obtain high purity,beta-pinene.

The process proposed for the separation of the alpha-pinene, beta-pinene, delta-3-carene fraction requires two batch distillation columns. The firs.t removes alpha-pinene at a 10:1 reflux ratio, steam distillation; the second separates a beta-pinene, delta-3-carene concentrate at a 30:1 reflux ratio, steam distillation, to obtain high purity beta-pinene and delta-3-carene plus a midfraction that is returned to the process as recycle..

An economic study of the process shows a 102.8 percent return bn an investment of $82,383 for a plant processing 2100 gallons of terpenes per. week. The payout time is 0.91 years. The plant and process described in this report would be economically feasible to build and operate.

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MONTANA STATE COLLEGE
Bozeman, Montana

December, 1964

ACKNOWLEDGEMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State College, and in particular Dr. Lloyd Berg, advisor and director of this research, for their encouragement, suggestions, and criticisms which have been so helpful in the successful completion of this project.

The author would also like to thank the management of the Waldorf-Hoerner Paper Products Company in Missoula, Montana for agreeing to supply raw materials and valuable information for this project.

The author would especially like to thank the National Institute of Health for its financial support of this project.

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ABSTRACT

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The basic raw material for this project was the crude sulfate turpentine from the Waldorf-Hoerner mill. The alpha-pinene and delta-3-carene content of the crude varies extensively over any given period of time, but the beta-pinene content remains quite constant at 10 percent of the crude.

Batch distillation was used as the method of separating the turpentine into pure components. The material most frequently used as a distillation charge for the project was a fraction of the crude turpentine consisting of 40.0 percent alpha-pinene, 4.5 percent camphene, 24.0 percent beta-pinene, and 31.5 percent delta-3-carene.

Gas chromatography was used for compound identification and determination of sample compositions.

The effects of column height, reflux ratio, and steam on the separation of the turpentine components were investigated. Scouting experiments showed that a 45 theoretical plate column operating at a 30:1 reflux ratio and steam distillation would have to be employed to obtain high purity beta-pinene.

The process proposed for the separation of the alpha-pinene, beta-pinene, delta-3-carene fraction requires two batch distillation columns. The first removes alpha-pinene at a 10:1 reflux ratio, steam distillation; the second separates a beta-pinene, delta-3-carene concentrate at a 30:1 reflux ratio, steam distillation, to obtain high purity beta-pinene and delta-3-carene plus a midfraction that is returned to the process as recycle.

An economic study of the process shows a 102.8 percent return on an investment of $82,383 for a plant processing 2100 gallons of terpenes per week. The payout time is 0.91 years. The plant and process described in this report would be economically feasible to build and operate.

INTRODUCTION

Montana was introduced to the pulp and paper industry in 1959 with the construction of a pulp mill in the Missoula, Montana area. The mill was built by the Waldorf-Hoerner Paper Products Company, and it utilizes the Kraft sulfate pulping process. The process is especially suited for pulping the softwood found in the northwestern United States.

The transformation from wood to pulp takes place in large cylindrical retorts called digesters. Here the action of heat, steam, pressure, and highly basic chemicals separate the cellulose fibers from wood chips by partially hydrolyzing the lignins and lower carbohydrates in the wood. When the pulp is discharged or "blown" from the digesters, a foul-smelling, condensable vapor is liberated (6). This vapor, when condensed, is called crude sulfate turpentine. The vapor, when not condensed, becomes an air pollutant.

The Waldorf-Hoerner mill produces 7000 gallons of crude sulfate turpentine weekly (3); since there is yet no industrial use for the material, the condensed turpentine becomes a liquid waste product which must be disposed of. The mill cannot profitably condense the crude turpentine until a use is found for the material and a market is established.

Waldorf crude sulfate turpentine consists essentially of five partially unsaturated cyclic hydrocarbons. The five compounds are

isomers of the molecular formula $C_{10}H_{16}$. Table 1 shows the structures of each of the isomers (4). An analysis of the crude turpentine is shown below. The analysis is not exact and is used here for illustration only.

Waldorf-Hoerner Crude Turpentine

Alpha-pinene	34%
Camphene	2%
Beta-pinene	10%
Delta-3-carene	42%
Dipentene	12%

Markets are available for all but delta-3-carene, and research is currently being conducted toward industrial application of that compound.

This research project is concerned with determining an economical process for recovering the beta-pinene from Waldorf crude sulfate turpentine. It is desired to use a distillation process that will yield beta-pinene of purity in excess of 90 percent.

Since beta-pinene is used as a starting material for many industrial processes, market availability does not present a problem. Linalool is made from beta-pinene and is used in floral perfumes and colognes. Citral, another product made from beta-pinene, has a lemon odor and is used in flavorings and perfumes. A process involving thermal isomerization and chlorination of beta-pinene yields citronellol which is used in the soap industry (1). The Glidden Chemical Company

supplies 40 percent of the United States market for levo-menthol with a complicated process using beta-pinene as the sole starting material (7).

The low percentage of beta-pinene in the crude sulfate turpentine suggests difficulty in obtaining a high yield of high purity beta-pinene. Although crude turpentines produced in other sections of the country have higher beta-pinene content (up to 22 percent), they will not be considered here (4). This project is directed exclusively to production of beta-pinene from Waldorf-Hoerner crude turpentine. This work is but one phase of a broad project underway for the purpose of producing a group of marketable, profitable products from the crude sulfate turpentine that is now being destroyed.

Distillation was chosen as the method of separating the turpentine components for two major reasons. First, it is the method most commonly employed to separate totally miscible organic liquids; second, previous research concerning the distillation of Waldorf crude turpentine had been conducted by Isaacson and McCumber (4 & 5); it was desired to follow their general plan of attack, since the ultimate plan is to unitize the total research into an economic industrial plant design.

Steam distillation found extensive application in this project because of the high boiling points of the terpene components. Since

water is immiscible with the crude turpentine, the partial pressures of each phase are additive, and the boiling temperature of the two phase system is less than that of pure water. Therefore, the high-boiling terpenes can be distilled at a boiling temperature below that of water. This prevents decomposition and polymerization of the terpenes, as well as effecting a better separation between components.

When a mixture of two or more components is distilled, a midfraction is nearly always obtained between any two pure components. Because terpenes are difficult to separate, as much as 20 percent of a crude turpentine charge must be taken off as midfraction. Since this amount of material cannot be economically discarded, the midfraction must be returned somewhere to the system as recycle. Much of this project is devoted to finding the optimum procedure for handling distillation midfractions as recycle.

Reflux ratio has a large effect on both the amount of midfraction obtained and the purity of the isolated components. It was anticipated that because of the low percentage of beta-pinene in the crude turpentine, a high reflux ratio will ultimately have to be used to obtain a good yield of high purity beta-pinene.

RESEARCH OBJECTIVES

The main objectives of this project were to determine the beta-pinene content of the Waldorf-Hoerner crude sulfate turpentine from Missoula, Montana; to obtain beta-pinene of purity comparable to that used by industry; to determine the optimum operating procedure and conditions necessary to produce the high purity beta-pinene; and to compile an economic evaluation of the process for industrial application.

Since production of beta-pinene from Waldorf-Hoerner crude turpentine necessarily meant separation from alpha-pinene and delta-3-carene, considerable attention was devoted to removing these two terpenes as high purity by-products.

EQUIPMENT AND MATERIALS

A. Distillation Equipment

During the first four months of the project, the distillation column used to attempt separation of beta-pinene from alpha-pinene and delta-3-carene was a four-foot glass cylinder of 1.0 inch diameter. To decrease heat loss from the column, the 1.0 inch cylinder was placed inside two other concentric glass cylinders of 2.0 and 3.0 inch diameters, respectively. The middle cylinder was wrapped with Nicrome wire as a heating coil. The 1.0 inch inner cylinder was equipped with ground glass joints (ball joint on bottom, taper join on top) to facilitate removable connections with the stillpot and condensing head.

The packing selected for the 1.0 inch inner cylinder was Fenske rings, one-eighth inch stainless steel helices. This particular packing was chosen because it has a high void content (about 50 percent), resists corrosion, and can be readily cleaned by many solvents, excluding strong acids. The column had approximately 25 theoretical plates.

When it was determined that the four-foot column would not allow the desired terpene separations, a three-foot section of column identical to the one described above was placed on top of the existing column. The columns were joined by using a taper joint-ball joint ground glass adapter. The adapter was also packed with Fenske rings and insulated

to incorporate the connection section as a part of the column. Calibration with a toluene-methylcyclohexane system showed that the column contained 45 theoretical plates.

A Corad head was used to serve the dual purpose of condensing the overhead product and establishing the desired reflux ratio. Although the head offers a variety of reflux ratios, 10:1, 20:1, and 30:1 were the ratios used for this project.

A two-liter flask was used for a stillpot because of the large liquid volume required for steam distillations. It was observed that atmospheric distillation could not be carried out in an open stillpot because of the combined influence of the high-boiling terpenes and the large amount of heat loss through the glass of the stillpot. In an effort to reduce the amount of heat loss, the stillpot was wrapped first with a layer of fiberglass insulation followed by an outside shield of heavy aluminum foil. The loss of heat was decreased sufficiently enough to allow atmospheric distillation of the terpenes.

Heating equipment for the stillpot and column consisted of heating mantles and Powerstats. A distillation equipment diagram is shown in Figure 1.

B. Analytical Equipment

The terpene samples taken throughout the entire project were analyzed for percentage compositions with a gas chromatograph

manufactured by the Wilkens Instrument and Research Company. The particular column used for terpene analysis was a six foot long steel tube packed with Ucon polar 50, HBJ-100 with a support made of Chromosorb P.

Chromatographic peaks were recorded on a Minneapolis-Honeywell recorder and the chromatograms were converted into percentage compositions with the use of a compensating polar planimeter.

It is of interest to note that a refractometer was not used for terpene analysis in this project. The major reason is that it is not possible to obtain completely pure terpenes from which standard weight percent solutions can be made for refractive index calibrations. The refractometer was used once when the number of theoretical plates of the distillation column were determined experimentally with a toluene-methylcyclohexane system.

C. Materials

The basic raw material used for this process was the crude sulfate turpentine from Waldorf-Hoerner. The beta-pinene content of this crude turpentine is low (average of 10 percent) compared to crude turpentines from pulp mills in other part of the country (4). The Missoula turpentine is unique in that it contains a high percentage of delta-3-carene. The presence of this compound caused a difficult separation problem which will be discussed at length in a following section.

Terpene samples needed for calibration, component identifications, and equilibrium studies were either impossible to obtain from outside sources or were of such low purity that they were too inaccurate to use for these purposes. High purity samples used for equilibrium data determinations were manufactured by the author.

RESULTS AND DISCUSSION

A. Exploratory Distillations

The first important step toward the separation of high purity beta-pinene from the crude sulfate turpentine was to determine at what reflux ratio and under what particular conditions the separation would be carried out.

Because beta-pinene lies between alpha-pinene and delta-3-carene with respect to boiling points, it was assumed that the separation problems encountered would be between beta-pinene and alpha-pinene and between beta-pinene and delta-3-carene. Since the two separations mentioned above were of primary interest, a mid-fraction of the crude turpentine consisting of alpha-pinene, beta-pinene, and delta-3-carene was used as the charge material for nearly all the distillations carried out during this project.

The separation capabilities of a distillation column under any given conditions were determined by sampling the overhead (distillate) and determining its composition by the gas chromatograph. The compositions thus determined were recorded on plots showing: percentage of component in distillate vs. percent distilled, with parameters of alpha-pinene, beta-pinene, and delta-3-carene.

The first separation attempt was a steam distillation in the 25 theoretical plate column described in the section on distillation equipment. The charge was the alpha-pinene, beta-pinene, delta-3-

carene fraction and the maximum available reflux ratio (30:1) was used. Table II gives a breakdown of the charge and the distillation results; all exploratory distillations were carried out in the same manner. The plot of this separation is shown in Figure 2. The plot of the first distillation disclosed at once what would prove to be the most difficult aspect of the project. The plot showed a rapid decrease in alpha-pinene as the beta-pinene began to come overhead, indicating an easy separation between alpha-pinene and beta-pinene. The beta-pinene purity rose to 85 percent but dropped off sharply due to the rapid follow-up of delta-3-carene. The plot indicated that the separation of beta- pinene from delta-3-carene would be difficult.

To determine what effect steam had on the first separation, a distillation was run in the 25 plate column at a 30:1 reflux ratio under atmospheric pressure; no steam was present. The maximum beta-pinene purity dropped to 65 percent because of a poorer separation between beta-pinene and delta-3-carene. An atmospheric distillation at a 20:1 reflux ratio decreased the maximum beta-pinene purity to 58 percent. The results of these two distillations are plotted in Figure 3 and Figure 4.

After this series of distillations, it was obvious that high purity beta-pinene could not be produced under the conditions used. Since steam distillation in the four-foot column at a 30:1 reflux

ratio did not produce a high purity beta-pinene product, the only alternative was to increase the number of theoretical plates. The eight-foot column described in the section on distillation equipment was constructed, increasing the number of theoretical plates to 45.

The first separation attempt with the 45 plate column was an atmospheric distillation at a 30:1 reflux ratio (Figure 5). With a maximum beta-pinene peak of 83 percent, the run was almost identical to the steam distillation at a 30:1 reflux ratio in the 25 plate column. The most noticeable effect of increased plates was the improved separation between beta-pinene and delta-3-carene. When a charge of the alpha-pinene, beta-pinene, delta-3-carene fraction was steam distilled at a 30:1 reflux ratio in the 45 plate column, the maximum beta-pinene purity was increased to greater than 90 percent. The results of this distillation are shown in Figure 6.

Up to this point, the practice of recycling distillation midfractions to obtain a higher yield of the desired product had not been attempted. When the midfractions taken from either side of the beta-pinene peak of the preceding run were added to a charge of the fraction and distilled, the width of the beta-pinene peak was noticeably widened (Figure 7). The plot illustrates the value of recycling midfractions.

B. Comparison of Beta-pinene Purities

For several months it was not known what beta-pinene purity would have to be reached to compete with beta-pinene already being produced in this country. Since The Glidden Company of Jacksonville, Florida is a large producer and consumer of beta-pinene produced from crude sulfate turpentine, their assistance was sought. Glidden sent an eight-ounce sample of beta-pinene labeled as 96 percent purity; comparison of chromatograms of Glidden's beta-pinene and the beta-pinene produced from Waldorf-Hoerner turpentine revealed that the purities of the two samples were nearly identical. The chromatograms of the two samples are shown in Figure 8. On the basis of the above comparison, it was assumed that the beta-pinene produced from the Waldorf-Hoerner crude turpentine was of a quality equal to that obtained from The Glidden Company.

C. Optimum Operation:

With the determination of beta-pinene of acceptable purity, attention was turned to the development of a process for production of the beta-pinene from the crude fraction consisting of alpha-pinene, beta-pinene, and delta-3-carene.

The crude fraction contained, for all purposes, the total amount of beta-pinene present in the crude sulfate turpentine. It also contained a high percentage of alpha-pinene and delta-3-carene. Further experiments indicated that a large amount of the alpha-

pinene could be removed by distilling the fraction under atmospheric pressure at a 10:1 reflux ratio. The high purity alpha-pinene overhead was taken off rapidly until beta-pinene became present in the distillate. The distillation was then stopped and the remainder (a concentrate of alpha-pinene, beta-pinene, and delta-3-carene) subjected to steam distillation at a 10:1 reflux ratio. Again high-purity alpha-pinene was taken off until beta-pinene became present in the distillate. Remaining in the stillpot was a desired concentrate of beta-pinene and delta-3-carene.

A charge of the beta-pinene, delta-3-carene concentrate was then steam distilled and 90 percent purity beta-pinene, 99 percent delta-3-carene, and a midfraction obtained as products. A breakdown of charge and product compositions for this run is given in Table III, and a plot of overhead composition vs. percent distilled is shown in Figure 9.

Using the midfraction from the previous distillation as recycle, a second charge of the beta-pinene, delta-3-carene concentrate was distilled to determine the effect of recycle on beta-pinene yield. Table IV gives a breakdown of charge and product compositions, and a plot of overhead compositions vs. percent distilled is shown in Figure 10. Comparison of Figure 9 and Figure 10 shows that the addition of recycle increased the yield of high purity beta-pinene. Comparison of Table III and Table

IV indicates that the volume of recycle did not increase.

At first glance, it seems that a reasonable process for breaking apart the alpha-pinene, beta-pinene, delta-3-carene fraction had been found. From the three-step distillation sequence, the final products were high purity alpha-pinene, beta-pinene, and delta-3-carene. Still, one phase of the process was wrong. The alpha-pinene content of the recycle from Run #14 (see Table III) was only 5.6 percent, while the alpha-pinene content of the recycle from Run #15 had increased to 8.4 percent (see Table IV). Alpha-pinene content was on the rise because the recycle was continually being added back to a charge of beta-pinene and delta-3-carene. Products of the subsequent distillation were beta-pinene, delta-3-carene, and recycle. Since no alpha-pinene was being removed from the cycle, the percentage of alpha-pinene would have continued to grow. It was decided to add the recycle back to the second distillation where high purity alpha-pinene was being taken as an overhead product.

Therefore the recycle from Run #15 was added to a charge of alpha-pinene, beta-pinene, delta-3-carene concentrate. The bottoms of this run (beta-pinene, delta-3-carene concentrate) were then distilled to obtain high purity beta-pinene, delta-3-carene, and recycle. It was hoped that the amount of alpha-pinene in the recycle would not increase. The conditions and results of these two runs are

given in Table V and Table VI. It can be seen that the midfraction recycle from Run #18 contained a lower percentage of alpha-pinene than the recycle from Run #16, which means the concentration of alpha-pinene will not increase with every distillation cycle.

From the data accumulated, an optimum distillation sequence for the alpha-pinene, beta-pinene, delta-3-carene fraction can be suggested. The process is best represented by a schematic diagram and is shown in Figure 11.

Distillation I of the schematic diagram is not of particular importance in this project. It is assumed that the alpha-pinene that can be removed by atmospheric distillation at a 10:1 reflux ratio will have been removed before the boundaries of this project are reached. An industrial process for the separation of high purity beta-pinene from a mixture of alpha-pinene, beta-pinene, and delta-3-carene will be designed around Distillation II and Distillation III of Figure 11. The extensive breakdown of experimental data given in Table V and Table VI correspond to Distillation II and Distillation III, respectively. A flow diagram for the proposed two-distillation recovery of beta-pinene is shown in Figure 12. Valves, pumps, and other necessary equipment are not shown in the simplified flow diagram.

D. Assumptions

Because the distillation project proposed in the previous section uses the alpha-pinene, beta-pinene, delta-3-carene fraction as a raw material, it is necessary to determine how much the composition will vary over any given period of time. The fraction spoken of here is obtained from a process that isolates alpha-pinene and delta-3-carene from the crude turpentine.

A year-long study of Waldorf crude turpentine revealed that the amount of alpha-pinene and delta-3-carene present varied extensively, but the beta-pinene content was always between 9 and 12 percent of the crude (5). If the beta-pinene content always remains this constant, the alpha-pinene, beta-pinene, delta-3-carene fraction will always have the same composition regardless of the variance of alpha-pinene and delta-3-carene content in the crude. If the crude turpentine is broken apart at a 10:1 reflux ratio, a certain amount of alpha-pinene and delta-3-carene will be removed with the beta-pinene, and the amounts will remain the same in the mid-fraction as long as the beta-pinene content does not vary. Therefore it is assumed that the composition of the alpha-pinene, beta-pinene, delta-3-carene fraction will remain constant over any given period of time.

As discussed earlier, the laboratory distillation columns are

packed with Fenske rings which results in a large column void volume. Because of the void volume, 60 to 70 milliliters of terpenes are left in the 45 plate column after any distillation. In laboratory-scale distillations, the holdup constitutes about 8 percent of the charge. It is assumed in this project that the amount of holdup becomes negligible as the volume of the stillpot charge is increased. In a commercial-scale operation where large volume charges and total-draining columns are used, the holdup problem becomes negligible.

ECONOMIC STUDY

With the proposal of an optimum distillation sequence for the alpha-pinene, beta-pinene, delta-3-carene fraction, it was necessary to determine the economic feasibility of the process. It should be stated at this time that this process is but one phase of a proposed plant for the isolation of high-purity terpenes from Waldorf-Hoerner crude sulfate turpentine. It was once believed that the beta-pinene could not be isolated in high enough purity to be marketable. This project has shown that high purity beta-pinene can be obtained along with high purity alpha-pinene and delta-3-carene as by-products. The next goal is to make the proposed process economical.

Most of the cost data, assumptions, and physical constants were taken from a design report compiled by Grose and Ness (3). Approximately 30 percent of the crude sulfate turpentine is the alpha-pinene, beta-pinene, delta-3-carene midfraction. Therefore 2100 gallons per week of the fraction is obtained at an average composition of 40.0 percent alpha-pinene, 4.5 percent camphene, 24.0 percent beta-pinene, and 31.5 percent delta-3-carene. It is assumed that the fraction has a value of $.40 per gallon. Selling prices for the high purity product streams are

alpha-pinene	$.30/gallon
beta-pinene	.70/gallon
delta-3-carene	5.00/gallon

The prices quoted for alpha-pinene and beta-pinene are well established; the price for delta-3-carene is less certain, but

market research indicates that it is reasonable. The column data for overhead and bottom products is taken from Table V of the Appendix and the economics correspond to the process shown in Figure 12.

A. Column Calculations

Column 1 $\frac{65 \text{ ml recycle}}{500 \text{ ml fresh fraction}}$ x 2100 gal. fresh fraction =

273 gal. recycle

(2100 + 273) gal. x $\frac{170}{565}$ = 714 gal./wk alpha-pinene overhead

(2100 + 273) gal. x $\frac{322 + 73}{565}$ = 1660 gal./wk beta-,delta-3 concentrate bottoms

Assume a 1.1 ratio of water taken over with terpenes

Assume a total operating time for columns of 110 hours/wk

Density terpene liquid = 7.33 lb/gal.
Density terpene vapor = 0.20 lb/ft^3.
Density water liquid = 8.33 lb/gal.
Density water vapor = 0.027 lb/ft^3.

Production rate of alpha-pinene

$714 \frac{\text{gal}}{\text{wk}} \times \frac{\text{week}}{110 \text{ hr}} \times 7.33 \frac{\text{lb}}{\text{gal}} = 47.7$ lb/hr alpha-pinene

$714 \times \frac{1}{110} \times 8.33 = 54.1$ lb/hr water

Total: 101.8 lb/hr overhead

Allowable vapor velocity

Average $d_V = \frac{0.2 \text{ lb/ft}^3 + 0.027 \text{ lb/ft}^3}{2} = .114$ lb/ft^3

Average $d_L = \frac{54.8 \text{ lb/ft}^3 + 62.4 \text{ lb/ft}^3}{2} = 58.6$ lb/ft^3

$u = .056 \sqrt{d_L/d_V} = .056 \sqrt{58.6/.114}$

$u = 1.27$ ft/sec

Vapor rate needed to produce 101.8 lb/hr

$$V = 101.8 \frac{lb}{hr} \times \frac{ft^3}{.114\ lb.} \times \frac{hr}{3600\ sec} \times 1.47$$

$$V = 0.365\ ft^3/sec$$

Column specifications

Reflux ratio = 10:1

Vapor rate = $.365(10 + 1) = 4.02\ ft^3/sec$

Column cross-section = $\frac{4.02\ ft^3/sec}{1.27\ ft/sec} = 3.16\ ft^2$

Diameter = 24.1 inches

Assume a plate efficiency of 75 percent.

Actual plates = $\frac{45}{.75} = 60$

Using a cost for a 30 inch column at $251.00 per plate,

$251 x 60 = $15,080

Column 1 costs $15,080

Column 2

1660 gal. x $\frac{77 + 37}{322 + 73}$ = 479 gal./wk beta-pinene overhead

1660 gal. x $\frac{65}{395}$ = 273 gal/wk midfraction overhead

1660 gal. x $\frac{117 + 36 + 60}{395}$ = 907 gal./wk delta-3-carene bottoms

479 + 273 = 752 gal./wk overhead in Column 2

Production rate of Column 2

752 $\frac{gal}{wk}$ x $\frac{week}{110\ hr}$ x 7.33 lb = 50.2 lb/hr terpene

752 x $\frac{1}{110}$ x 8.33 = 57.0 lb/hr water

Total: 107.2 lb/hr overhead

Allowable vapor velocity

$$u = .056 \sqrt{58.6/.114} = 1.27 \text{ ft/sec}$$

Vapor rate needed to produce 107.2 lb/hr

$$V = 107.2 \frac{\text{lb}}{\text{hr}} \times \frac{\text{ft}^3}{.114 \text{ lb}} \times \frac{\text{hr}}{3600 \text{ sec}} \times 1.47$$

$$V = 0.384 \text{ ft}^3/\text{sec}$$

Column 2 specifications

Reflux ratio = 30:1

Vapor rate = $.384 (30 + 1) = 11.90 \text{ ft}^3/\text{sec}$

Column cross-section = $\frac{11.90 \text{ ft}^3/\text{sec}}{1.27 \text{ ft/sec}} = 9.37 \text{ ft}^2$

Diameter = 41.0 inches

Actual plates = 60

Using a cost for a 41 inch column at $315.00 per plate,

$315 x 60 = $18,900

Column 2 costs $18,900

B. Condenser Calculations

Assumptions:		
	Cooling water to condenser	40°F
	Cooling water out of condenser	110°F
	Terpenes out of condenser	203°F
	Condensing area heat transfer coeff.	150
	Cooling area heat transfer coeff.	115

Column 1

Heat duty for condensing

$$\frac{(714 \text{ gal/wk})(7.33 \text{ lb/gal})(123.5 \text{BTU/lb})(10+1)}{110 \text{ hr/wk}} \text{ (for terpenes)}$$

$$+ \frac{(714)(8.33)(970)(10+1)}{110} \text{ (for water)}$$

$= 65,000 + 583,000$

$= 648,000$ BTU/hr

Heat duty for cooling product 5 degrees

$$\frac{(364)(7.33)(.411)(5)(10+1)}{110}$$

$= 2260$ BTU/hr

Total heat duty $= 648,000 + 2260 = 650,260$ BTU/hr

Temperature of water entering condenser zone

$$T = 40 + (110 - 40)\ \frac{2,260}{650,260} = 40.4^{\circ} = F$$

Log mean temperature difference

$$(\Delta T)_{lm} = \frac{(203 - 110) - (198 - 40.4)}{\ln \frac{203 - 110}{198 - 40.4}} = 103^{\circ}F$$

Area for condensing $= \frac{650,260}{(103)(150)} = 42.3\ ft^2$

Area for cooling $= \frac{2260}{(103)(115)} = 0.19\ ft^2$

Total condenser area $= 42.3 + .19 = 42.49\ ft^2$

Condenser cost $= \$920.00$

Column 2

Heat duty for condensing

$$\frac{(752)(7.33)(123.5)(30+1)}{110} + \frac{(752)(8.33)(970)(30+1)}{110}$$

$= 403,000 + 3,590,000 = 3,993,000$ BTU/hr

Heat duty for cooling product 5 degrees

$$\frac{(752)(7.33)(.411)(5)(30+1)}{110}$$

$= 6680$ BTU/hr

Total heat duty = 3,993,000 + 6,680 = 3,999,680 BTU/hr

Temperature of water entering condenser zone

$T = 40.4°F$

Log mean temperature difference

$(\Delta T)_{lm} = 103\ °F$

Area for condensing = $\frac{3,999,680}{(103)(150)} = 337.0\ ft^2$

Area for cooling = $\frac{6,680}{(103)(115)} = 0.56\ ft^2$

Total condenser area = $337.56\ ft^2$

Condenser cost = $1685.00

C. Steam Cost

$$\text{Cost} = P\,(r+1)(1.33)\frac{H}{1000} \times \frac{U}{1000}$$

$$= (101.8\ \tfrac{lb}{hr})(110\ \tfrac{hr}{wk})(10+1)(1.33)\left(\frac{864}{1000}\right)\left(\frac{\$.50}{1000}\right)$$

$$+(107.2)(110)(30+1)(1.33)\left(\frac{864}{1000}\right)\left(\frac{\$.50}{1000}\right)$$

= $70.5/week + $204.0/week = $274.50/week

D. Equipment Schedule

Steam distillation columns

One 60 plate column, 24.1 inch diameter, R251.00/plate	$15,080.00
One 60 plate column, 41.0 inch diameter, R315.00 plate	18,900.00

Condensers

One 42.49 ft^2 heat transfer area	920.00
One 337.6 ft^2 heat transfer area	1,685.00

Kettles (Stillpots)		
One with 2500 gallon capacity		700.00
One with 1500 gallon capacity		500.00
Pumps		(est.) 1,500.00
Storage		
3000 gal. α, B, Δ-3 storage	$590	
1000 gal. alpha- storage	500	
500 gal. beta- storage	400	
1000 gal. delta-3- storage	500	
500 gal. recycle storage	400	2,390.00
Total Equipment Cost		$40,630.00

E. Economic Balance

Total equipment cost	$40,630.00
Installation at 10% of equipment	4,063.00
Engineering at 5%	2,032.00
Instrumentation at 10%	4,063.00
Piping at 10%	4,063.00
Wiring at 5%	2,032.00
Building	5,000.00
Plant Investment	$61,883.00

Weekly operating costs

Raw material	2100 gal. at $.40/gal.	$840.00
Utilities	$1000/year	19.00
Labor	1 man, 3 shifts, $2.50/hr	420.00
Taxes and insurance at 3% of plant investment		36.00
Depreciation at 10% of plant investment		119.00
Steam cost		274.50
		$1,708.50

Working capital (3 months operating costs) $20,500.00

Total investment = plant invest. + working cap.
= 61,883.00 + 20,500.00 82,283.00

Total receipts

alpha-pinene	714 gal.	at $.30	= $214.00
beta-pinene	479 gal.	at $.70	= 335.00
delta-3-carene	907 gal.	at $5.00	= 4530.00

Yearly expenses

52 x $1708.00 = $88,800

Gross Receipts

50 x $5079.00 = $254,000

Gross profit

254,000 - 88,800 = $165,200

Taxes (Federal income)

(25,000)(.30) + (140,200)(.52) = $80,500

Net profit

165,200 - 80,500 = $84,700

Return on investment = net profit/total investment

84,700/82,383

= 102.8%

Payout time = total investment/(net profit + depreciation)

82,383/(84,700 + 6190)

= 0.91 years

CONCLUSIONS

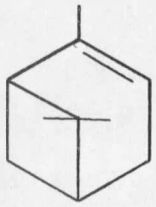
The data presented in this report shows that beta-pinene can be economically extracted from Waldorf-Hoerner crude sulfate turpentine. The proposed plant would process 2100 gallons of alpha-pinene, beta-pinene, delta-3-carene fraction weekly. Using the suggested selling price for delta-3-carene of $5.00 per gallon, the plant gives 102.8 percent return on an investment of $82,383 and a payout time of 0.91 years. It should be noted that the process is economically feasible only if alpha-pinene and delta-3-carene are removed as high-purity by-products.

The plant and process proposed here would break even for a delta-3-carene selling price as low as $1.30 per gallon. If the delta-3-carene was sold for $2.00 per gallon, the return on investment would be 23 percent and the payout time would be 3.26 years. It can be seen that the proposed process would be economically feasible even if the original proposed selling price for delta-3-carene was found to be too high.

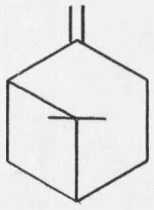
Because of the favorable economics of the proposed process, it is probable that the Waldorf-Hoerner pulp and paper mill at Missoula, Montana will become an industrial source of beta-pinene and other valuable terpene products.

APPENDIX

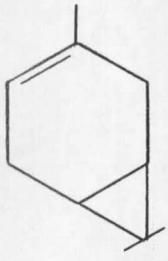
TABLE I. Components of Crude Sulfate Turpentine



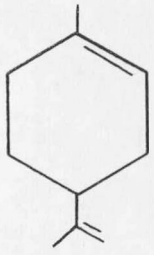
Alpha-pinene



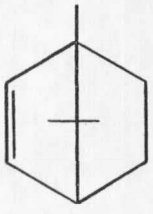
Beta-pinene



Delta-3-carene



Dipentene



Camphene

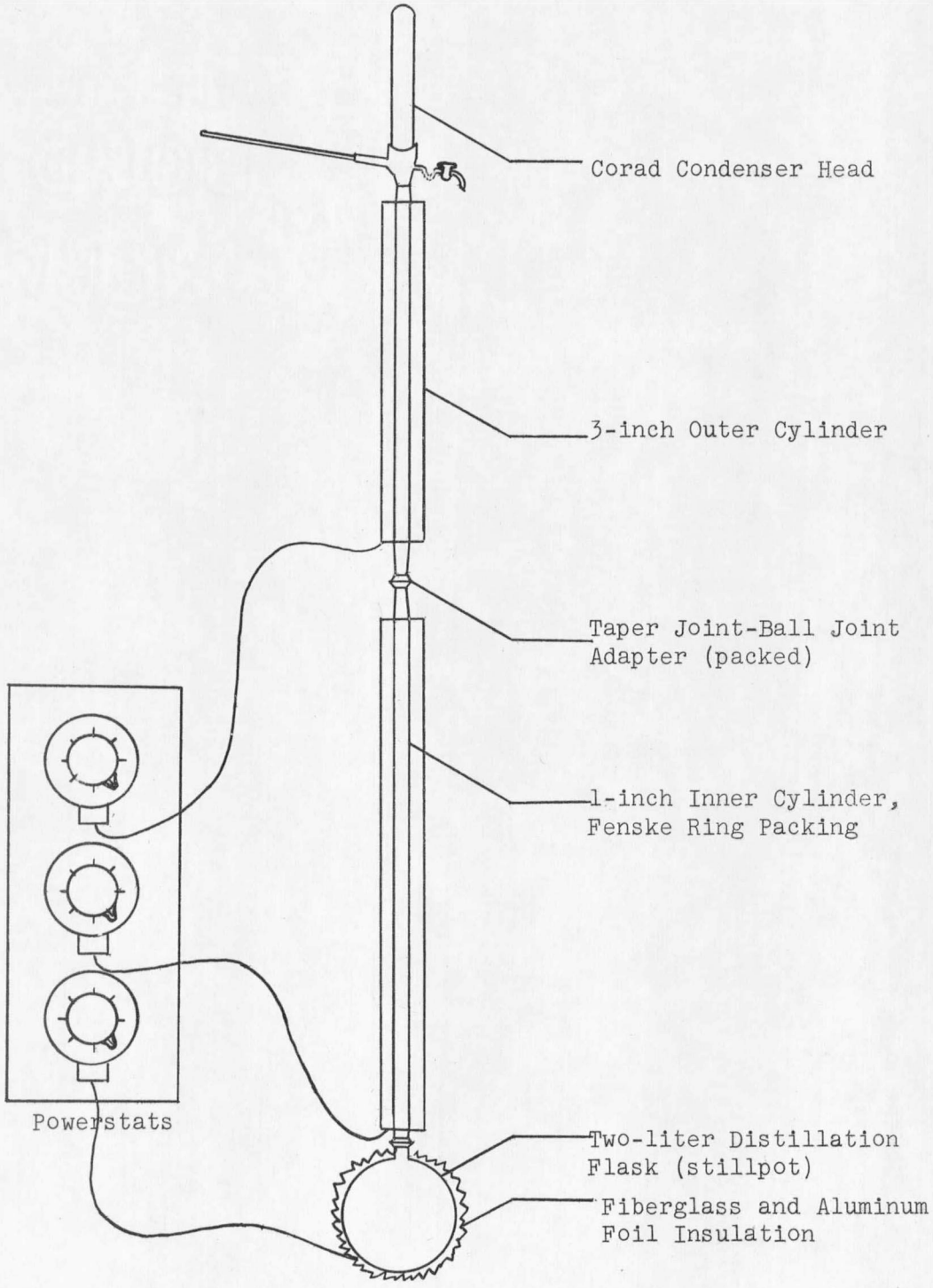


Figure 1. Distillation Apparatus

TABLE II. Conditions and Results of a Typical Distillation Run

Run #1

30:1 reflux ratio, steam distillation

Charge: 300 milliliters of alpha-pinene, beta-pinene, delta-3-carene fraction

Composition: 36.9 % alpha-pinene
24.2 % beta-pinene
38.8 % delta-3-carene

Cut	Volume	Composition	Still Temp.	Column Temp.	Top Temp.
1	20	99% alpha	96	86	80
2	20	99% alpha	96	86	90
3	20	97% alpha	96	86	90
4	21	91.5% alpha 4.2% beta	105	86	90
5	22	90.5% alpha 4.9% beta	103	86	90
6	9	37.5% alpha 54.2% beta	102	86	90
7	12	8.5% alpha 81.0% beta 8.5% delta-3	102	86	90
8	12	3.1% alpha 85.5% beta 11.5% delta-3	102	86	91
9	9	78.6% beta 21.4% delta-3	100	86	91
10	15	61.3% beta 38.7% delta-3	100	86	91
11	9	41.2% beta 58.8% delta-3	100	86	92

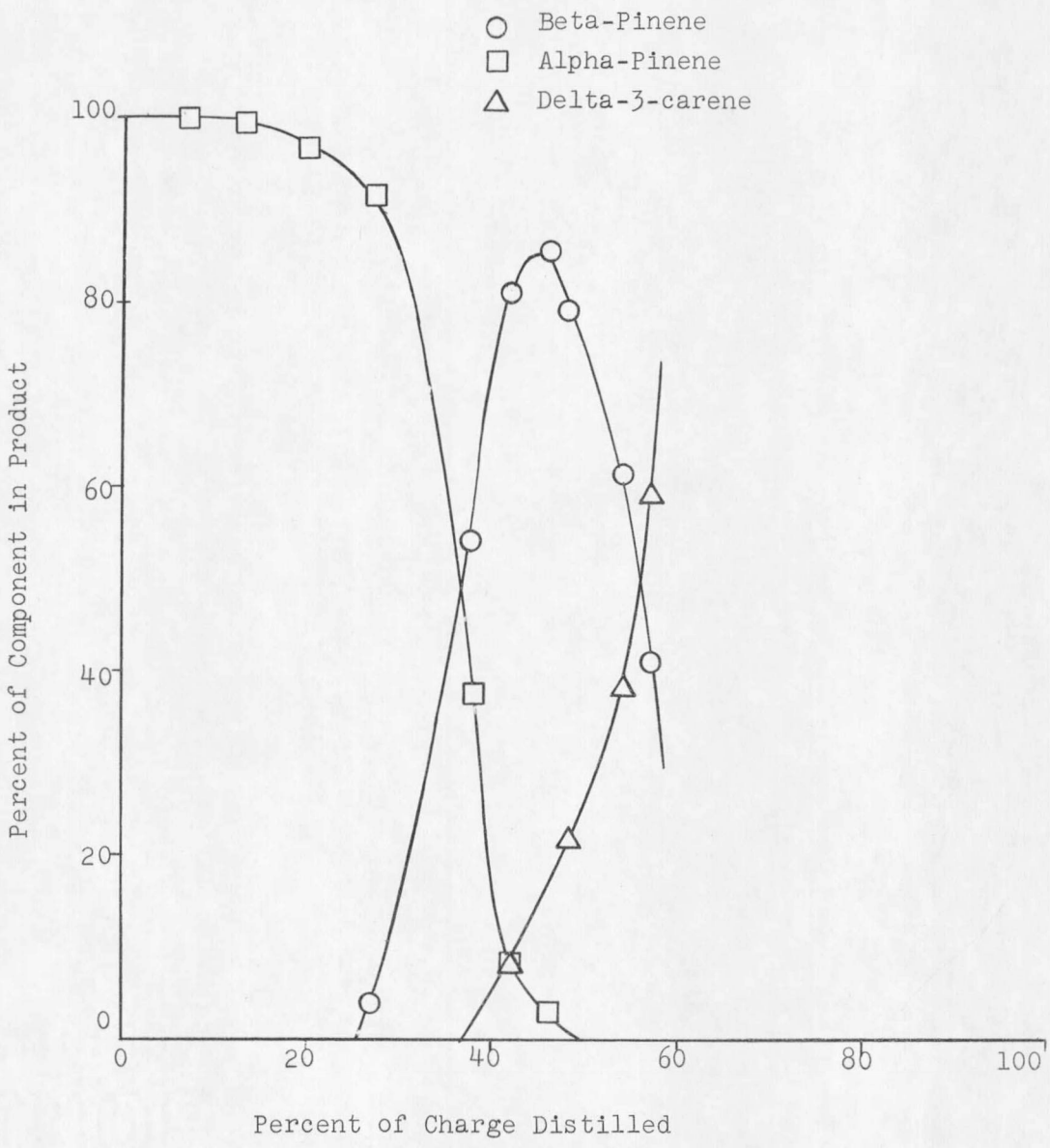


Figure 2: Run #1; Steam Distillation of the Alpha-pinene, Beta-pinene, Delta-3-carene Fraction, 30:1 Reflux Ratio.

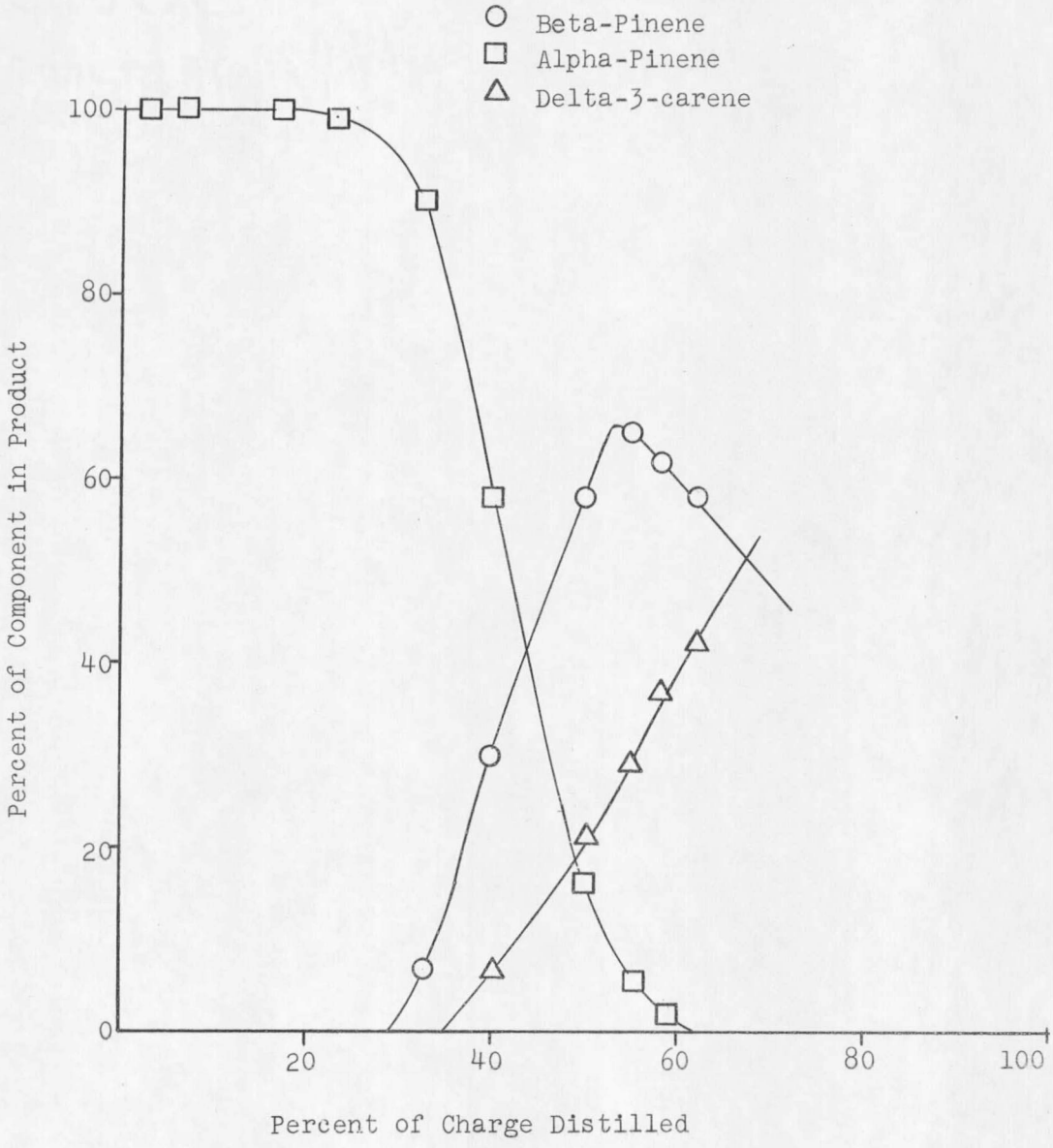


Figure 3: Run #4; Atmospheric Distillation of the Alpha-pinene, Beta-pinene, Delta-3-carene Fraction with 25 Plates, 30:1 Reflux Ratio

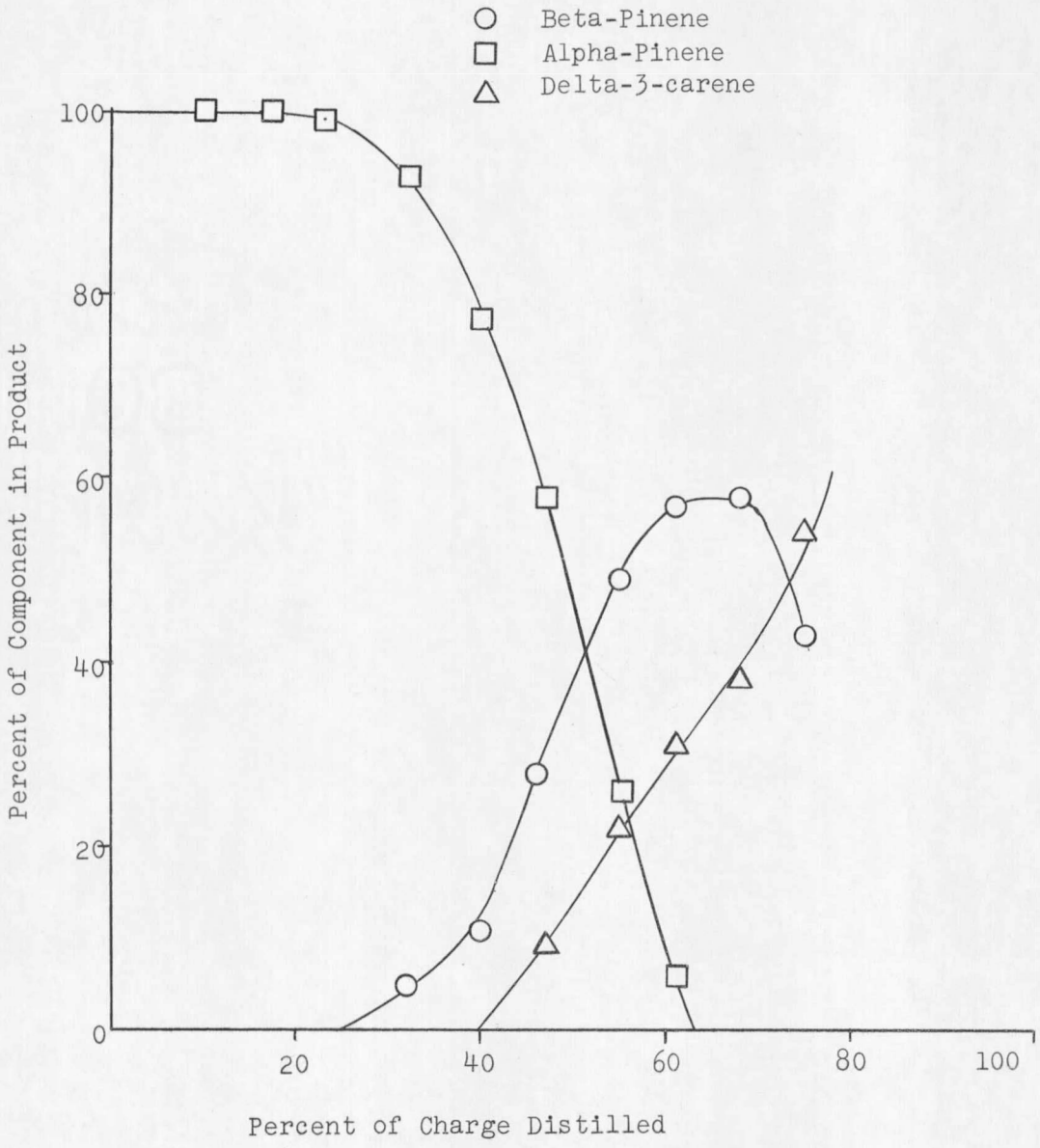


Figure 4: Run #5; Atmosphere Distillation of the Alpha-Pinene, Beta-pinene, Delta-3-carene Fraction with 25 Plates, 20:1 Reflux Ratio.

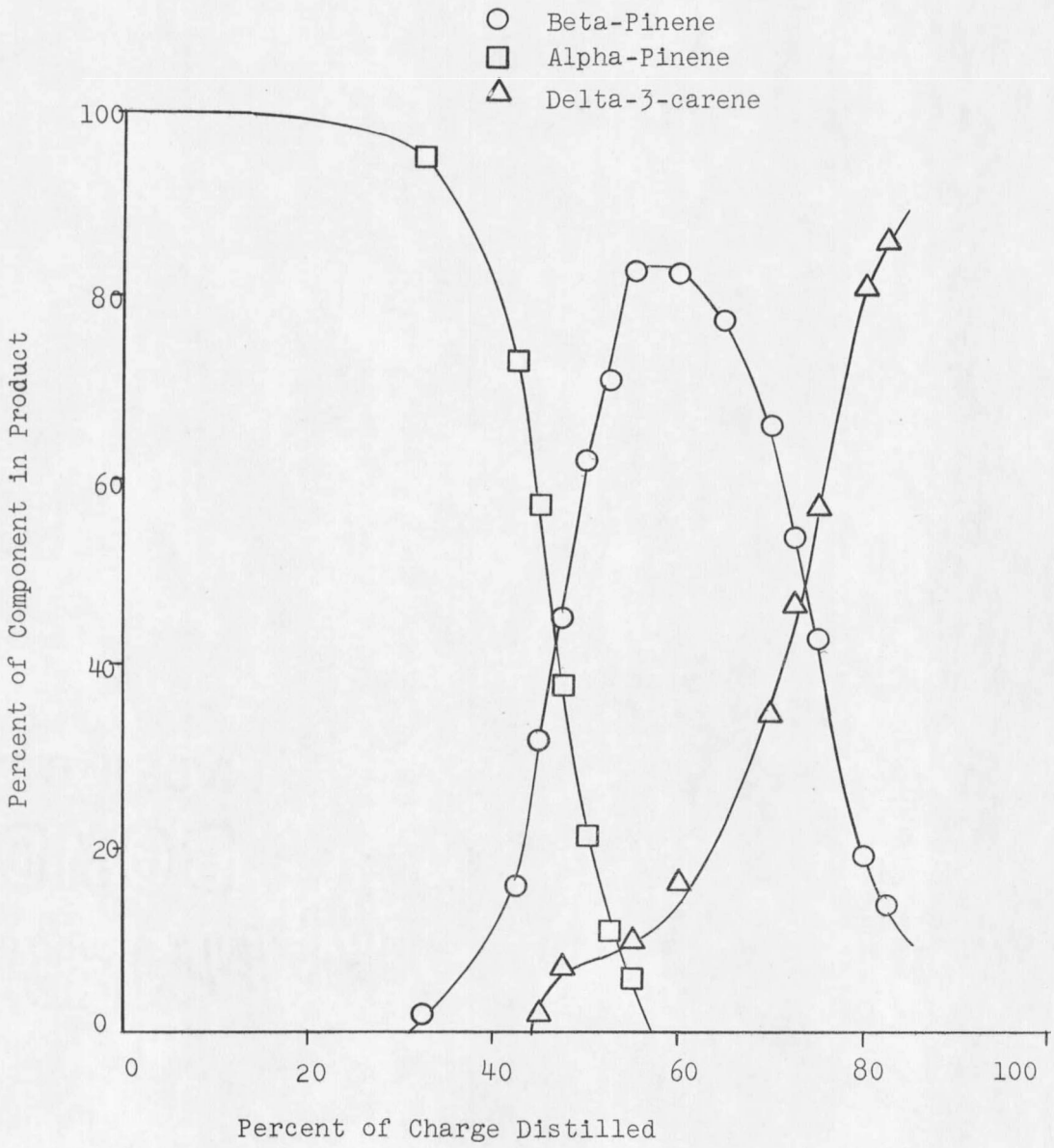


Figure 5: Run #7; Atmospheric Distillation of the Alpha-pinene, Beta-pinene, Delta-3-carene Fraction with 45 Plates; 30:1 Reflux Ratio.

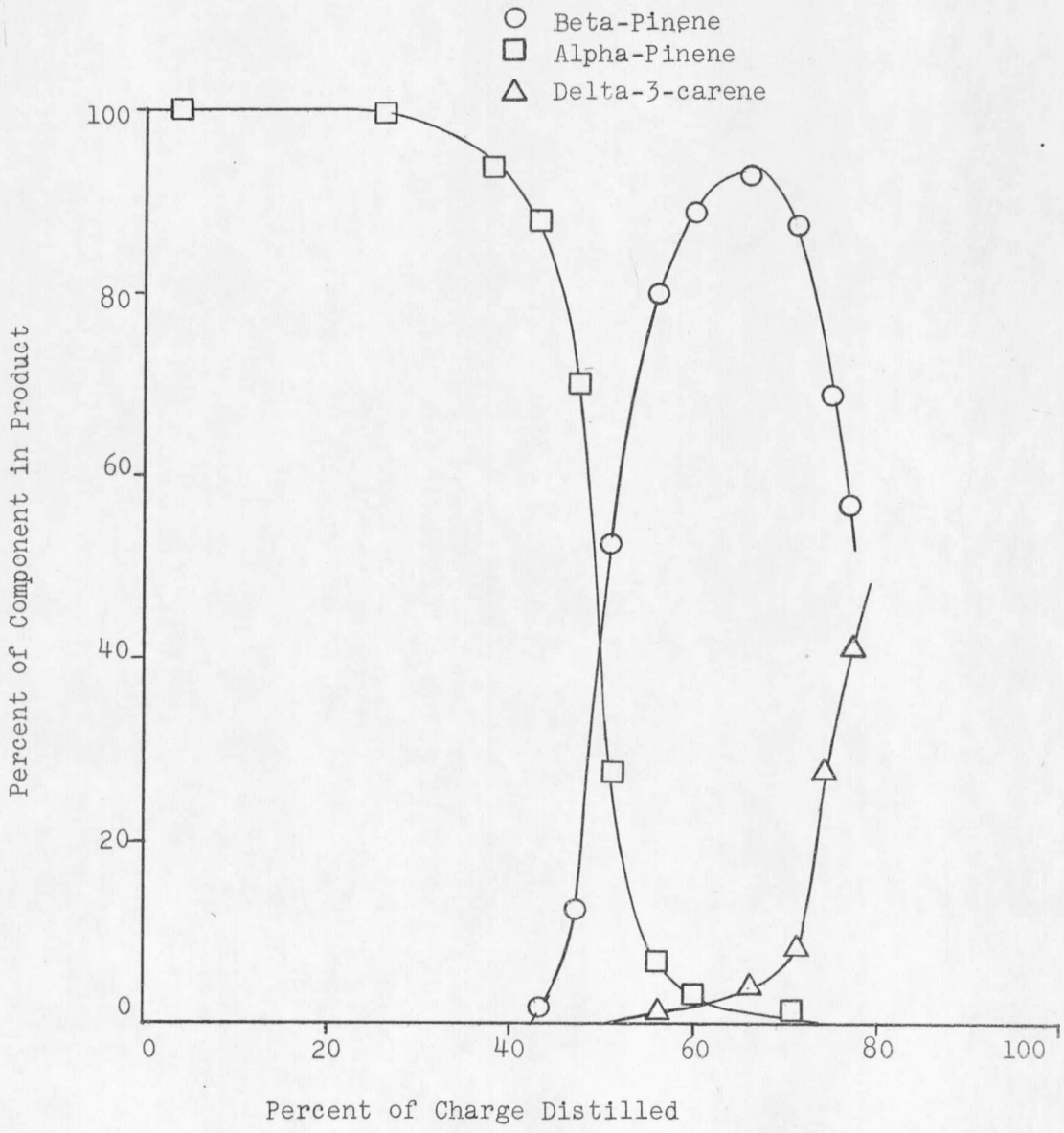


Figure 6: Run #9, Steam Distillation of the Alpha-pinene, Beta-pinene, Delta-3-carene Fraction with 45 Plates, 30:1 Reflux Ratio.

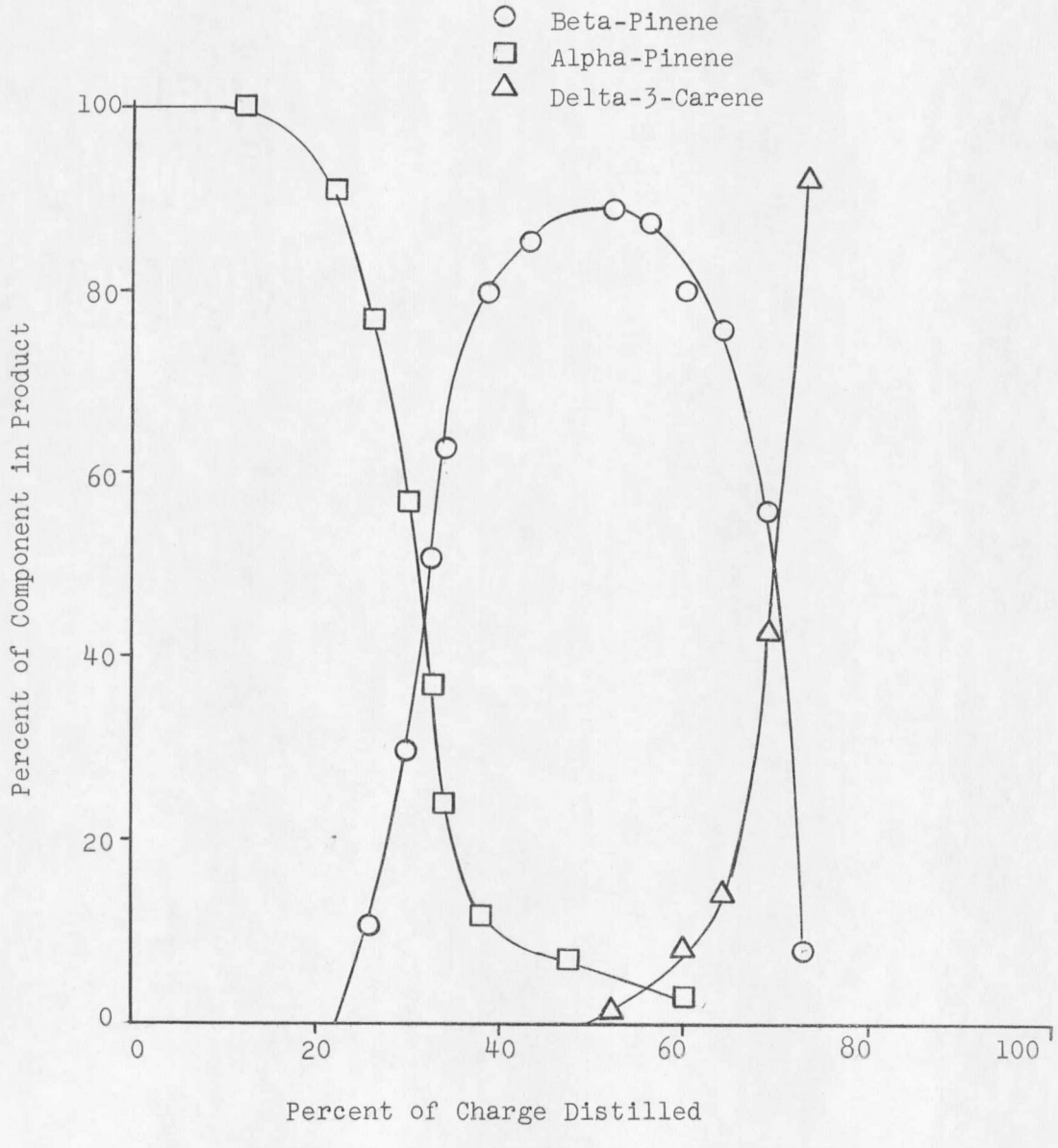


Figure 7: Run #10, Steam Distillation of the Alpha-pinene, Beta-pinene, Delta-3-carene Fraction with 45 Plates, 30:1 Reflux Ratio, and Recycle Added.

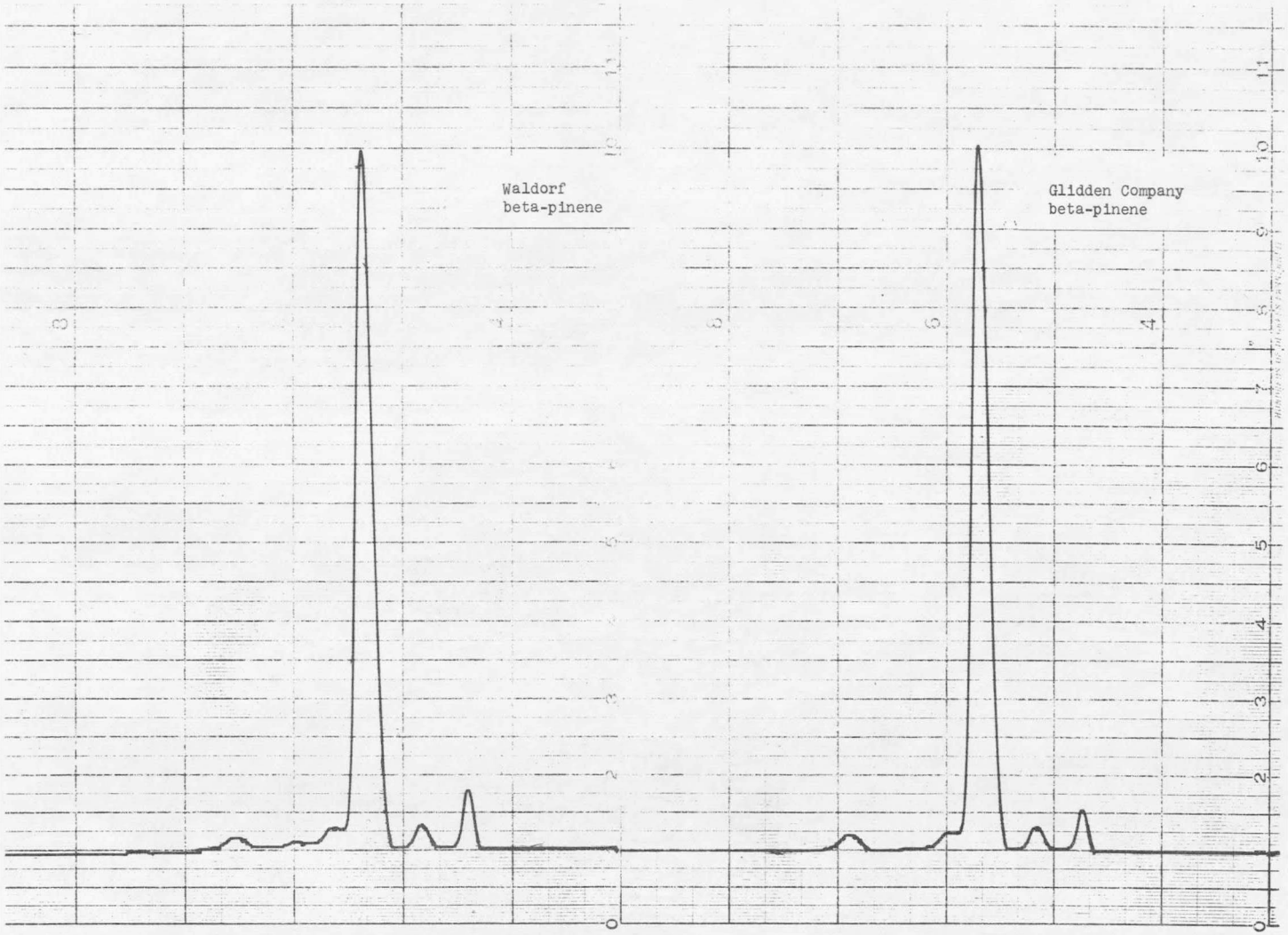


Figure 8: Comparison of the Chromatograms of Beta-pinene produced by the Glidden Co. and Beta-pinene produced from Waldorf Turpentine.

TABLE III. Conditions and results for the Distillation of Beta-pinene, Delta-3-carene concentrate

Run #14

Charge: 300 ml beta-, △-3 carene concentrate

Composition:
1.9% alpha-pinene
0.6% camphene
37.0% beta-pinene
60.5% △-3 carene

400 ml H_2O

Reflux ratio: 30:1 & 20:1

Products: 60 ml beta-pinene

Composition:
4.1% alpha-pinene
0.9% camphene
92.0% beta-pinene
2.9% △-3 carene

75 ml recycle (midfraction)

Composition:
5.6% alpha-pinene
5.6% camphene
60.5% beta-pinene
28.3% △-3 carene

126 ml delta-3-carene (bottoms)

Composition: 99+ % △-3 carene

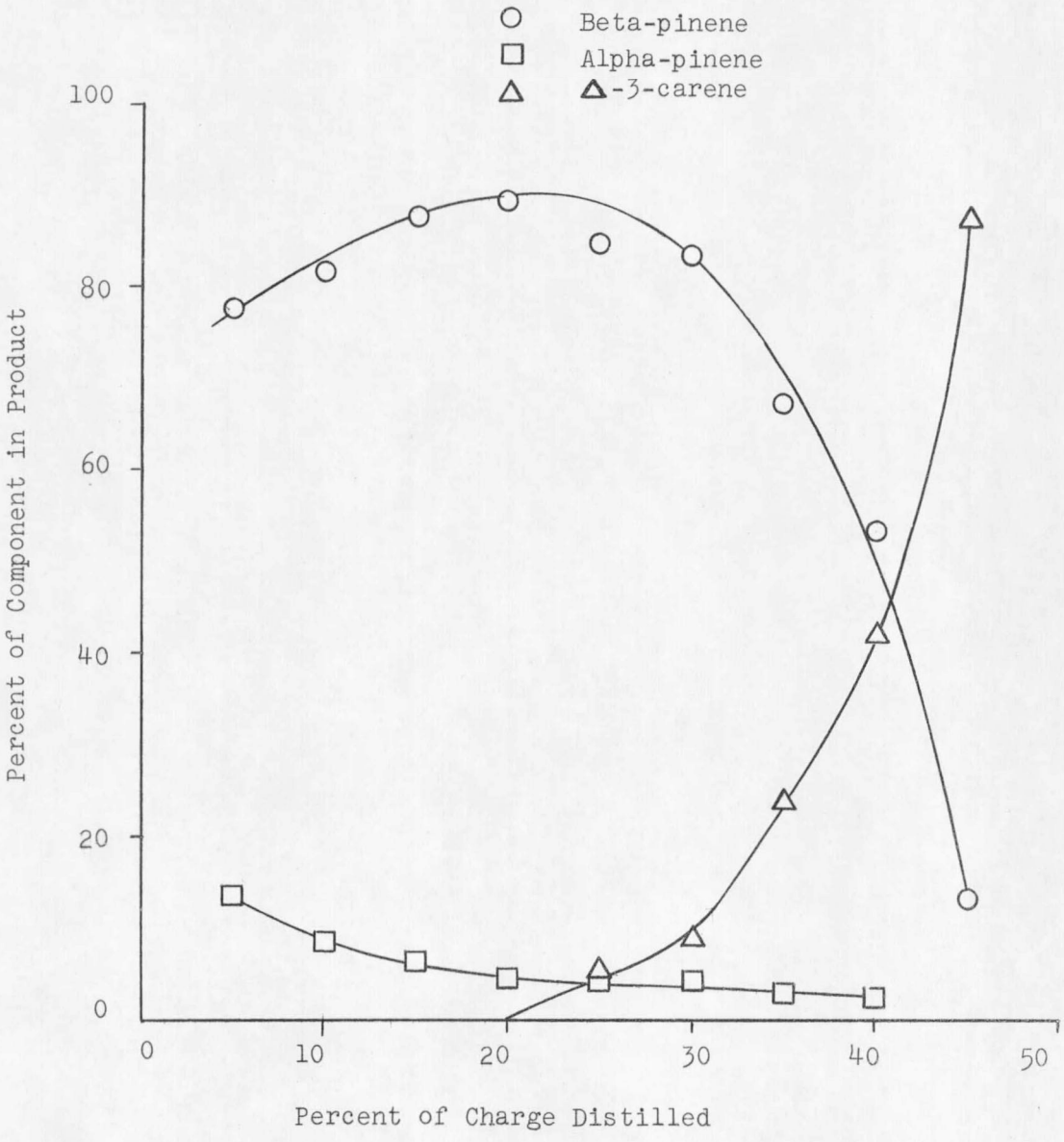


Figure 9: Run #14; Steam Distillation of the Beta-pinene, Delta-3-carene Concentrate.

TABLE IV. Conditions and Results for the Distillation of Beta-pinene, Delta-3-carene Concentrate with Recycle Added.

Run #15

Charge: 225 ml beta,△-3 concentrate
75 ml recycle from Run #14
300 ml terpenes

400 ml H_2O

Reflux Ratio: 30:1 & 20:1

Products: 75 ml beta-pinene

Composition: same as in Run #14

75 ml recycle

Composition: 8.4% alpha-pinene
3.8% camphene
64.4% beta-pinene
23.4% △-3 carene

110 ml delta-3-carene (bottoms)

Composition: 99+% △-3 carene

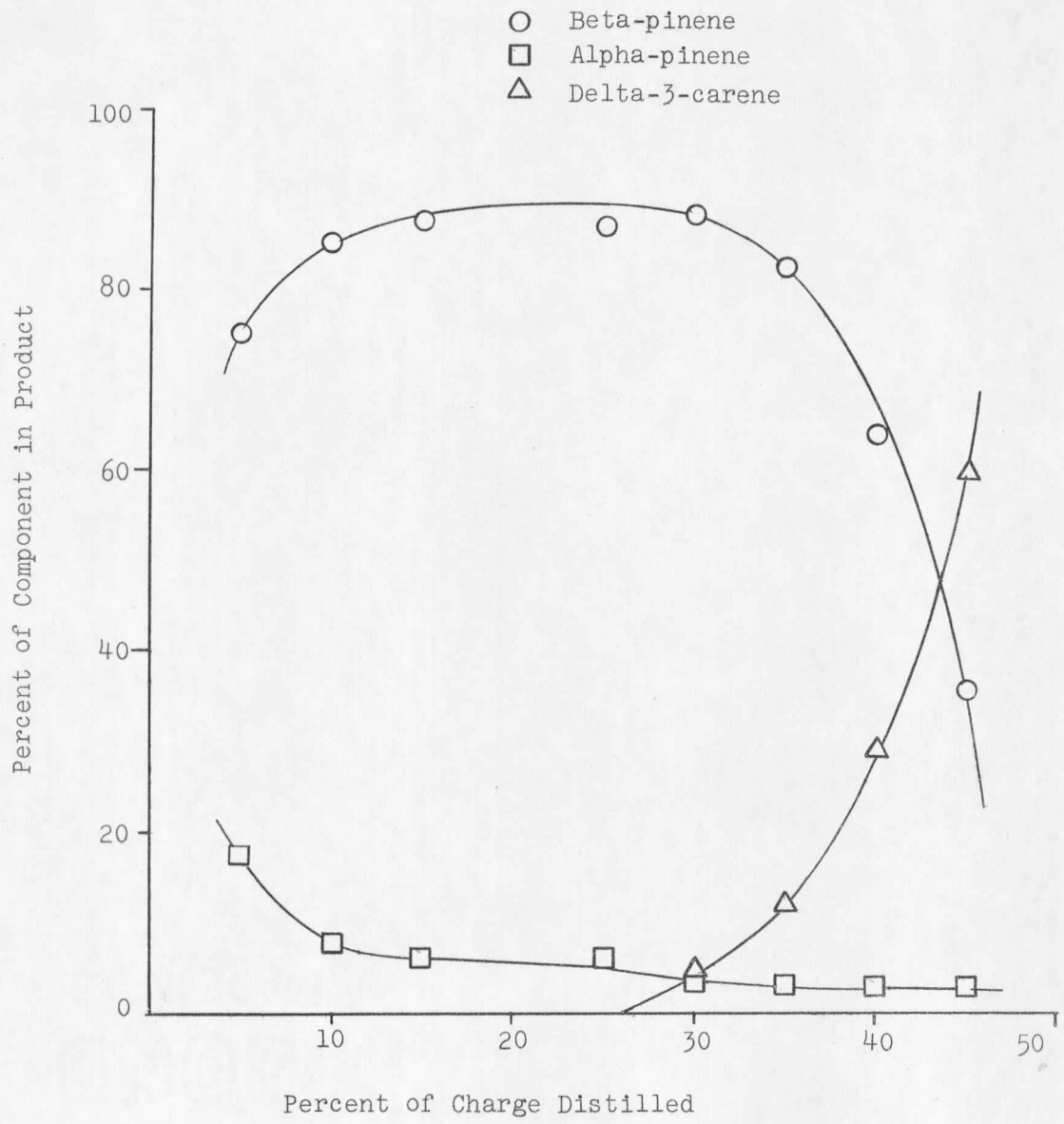


Figure 10: Run #15; Steam Distillation of the Beta-pinene, Delta-3-carene Concentrate with Recycle Added.

TABLE V. Conditions and Results for Optimum Distillation of Alpha-pinene, Beta-pinene, Delta-3-carene Concentrate

Run #17

10:1 reflux ratio, steam distillation

Charge: 500 ml alpha, beta-, △ -3 carene concentrate

Composition: 40.0% alpha-pinene
4.5% camphene
24.0% beta-pinene
31.5% △-3-carene

65 ml recycle from Run #15

Composition: 8.4% alpha-pinene
3.8% camphene
64.6% beta-pinene
23.4% △ -3 carene

Charge: 565 ml terpenes

Composition: 35.8% alpha-pinene
4.0% camphene
30.5% beta-pinene
29.8% △-3 carene

Removed: 170 ml tops (alpha-pinene)

Composition: 88.9% alpha-pinene
8.3% camphene
2.8% beta-pinene

322 ml bottoms △ -3 carene (bottoms)

Composition: 2.2% alpha-pinene
1.8% camphene
42.3% beta-pinene
53.7% △ -3 carene

TABLE VI. Conditions and Results for Optimum Distillation of Beta-pinene, Delta-3-carene Concentrate

Run #18

30:1 reflux ratio, steam distillation

Charge: 322 ml beta-, Δ-3 carene concentrate

Composition:	
2.2%	alpha-pinene
1.8%	camphene
42.3%	beta-pinene
53.7%	Δ -3 carene

Removed: 77 ml beta-pinene

Composition:	
4.1%	alpha-pinene
0.9%	camphene
92.0%	beta-pinene
2.9%	Δ -3 carene

65 ml recycle

Composition:	
5.7%	alpha-pinene
2.9%	camphene
57.9%	beta-pinene
33.9%	Δ -3 carene

117 ml bottoms Δ - 3 carene (bottoms)

Composition: 99+% Δ -3 carene

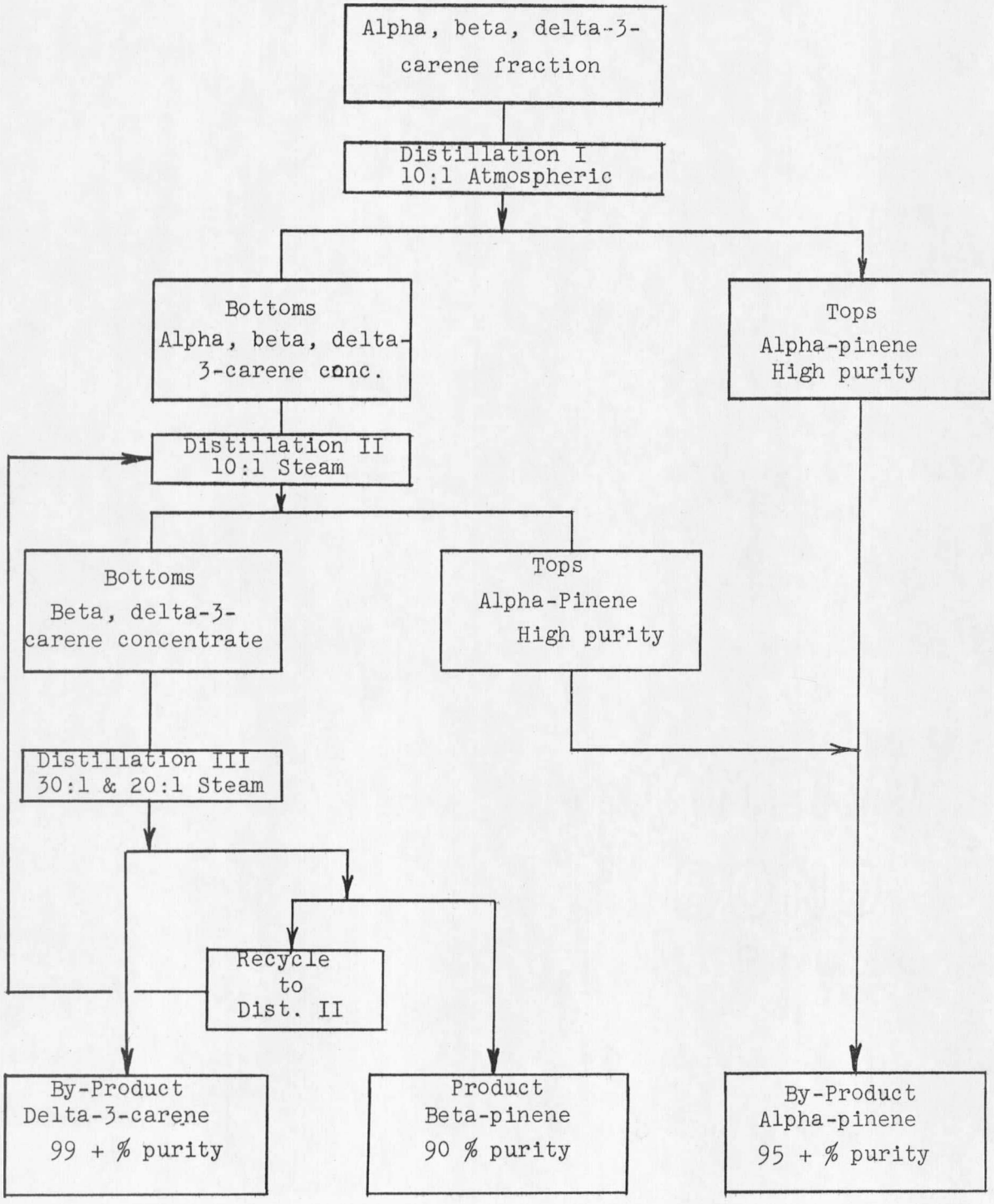


Figure 11. Optimum Distillation Process for the Alpha-pinene, Beta-pinene, Delta-3-carene Fraction.

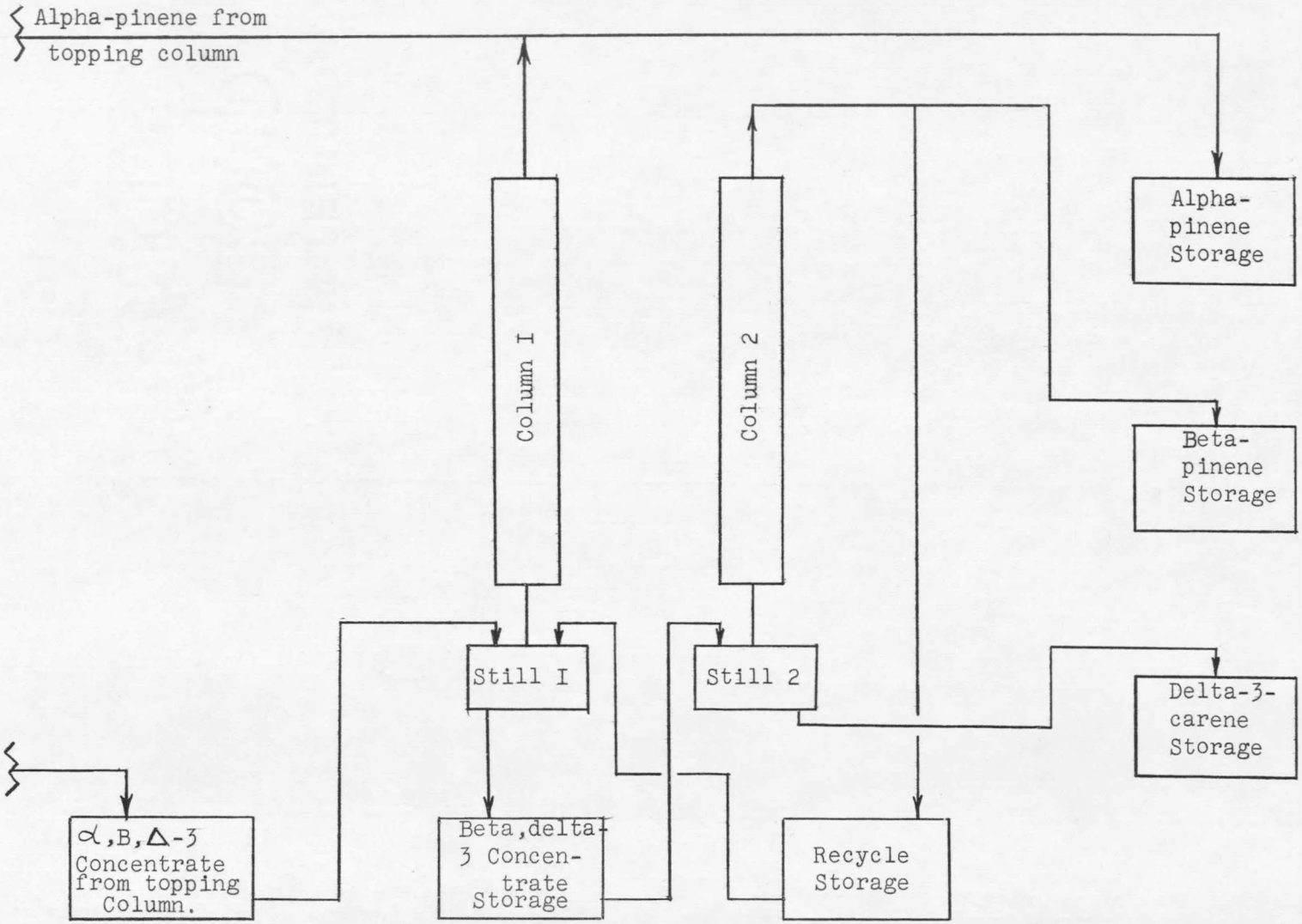


Figure 12. Flow Diagram of Proposed Beta-pinene Recovery Process.

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4. Isaacson, W. B., "Hydrodesulfurization of Crude Turpentine," Ph.D. Thesis, Montana State College, 1963.

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7. "Terpene Process Cools Erratic Menthol Supply, "Chemical Engineering, April 16, 1962, p. 80.