



Delta-3-carene recovery from crude sulfate turpentine  
by Harvey ThomasMcCumber

A thesis submitted to the Graduate faculty in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE in Chemical Engineering  
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Abstract:

This investigation was performed to study the feasibility of recovering terpene chemicals, primarily delta-3-carene, from crude sulfate turpentine produced at the Waldorf-Hedner Paper Products Company pulp mill in Missoula, Montana. The experimental apparatus consisted mainly of a distillation column, a Corad condensing head, and a gas chromatograph.

The crude sulfate turpentine from Missoula, Montana was analyzed and compared with turpentine samples from other sources and with those reported in the literature. The subject turpentine was found to contain an abnormally high percentage of delta-3-carene, a terpene chemical that is practically unknown in turpentine streams from pulp mills in the United States. Although there were considerable deviations in the quantity, of the chemical present in samples taken over approximately a one-year period, with special emphasis on weekly samples representing two consecutive months operations, the crude turpentine was found to contain an average of 40 percent delta-3-carene. -Due to the large quantity of the chemical available from this source\* and its otherwise relative rarity\* special emphasis was placed on the recovery of a high purity delta-3-carene product. Laboratory work was done to establish the operating conditions necessary to effect this recovery and to prepare high purity samples to be used in a preliminary market survey. Distillation runs, by atmospheric and steam methods, were made with columns of 6, 12, 18, and 24 theoretical plates operating at reflux ratios ranging from 2.5:1 to 20:1. It was found that the azeotropic mixtures of water and terpene enhanced the separation process and produced a product which was superior in odor and color characteristics. Ninety-five percent pure delta-3-carene can be recovered, by the use of a .24 theoretical plate column operated, with steam at a reflux ratio of 20:1.

. An economic analysis of the process based on the laboratory, data indicated that significant return on investment would be obtainable if an adequate market for the delta-3-carene could be developed. At a selling price of \$2.60 per gallon for the 95 percent pure delta-3-carene, a return on investment of 50 percent could be realized.

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HARVEY THOMAS McCUMBER

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Approved:

*Lloyd Bengtson*

Head, Major Department

*Lloyd Bengtson*

Chairman, Examining Committee

*James W. Smith*

Dean, Graduate Division

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## ABSTRACT

This investigation was performed to study the feasibility of recovering terpene chemicals, primarily delta-3-carene, from crude sulfate turpentine produced at the Waldorf-Hoerner Paper Products Company pulp mill in Missoula, Montana. The experimental apparatus consisted mainly of a distillation column, a Corad condensing head, and a gas chromatograph.

The crude sulfate turpentine from Missoula, Montana was analyzed and compared with turpentine samples from other sources and with those reported in the literature. The subject turpentine was found to contain an abnormally high percentage of delta-3-carene, a terpene chemical that is practically unknown in turpentine streams from pulp mills in the United States. Although there were considerable deviations in the quantity of the chemical present in samples taken over approximately a one-year period, with special emphasis on weekly samples representing two consecutive months' operations, the crude turpentine was found to contain an average of 40 percent delta-3-carene. Due to the large quantity of the chemical available from this source, and its otherwise relative rarity, special emphasis was placed on the recovery of a high purity delta-3-carene product. Laboratory work was done to establish the operating conditions necessary to effect this recovery and to prepare high purity samples to be used in a preliminary market survey. Distillation runs, by atmospheric and steam methods, were made with columns of 6, 12, 18, and 24 theoretical plates operating at reflux ratios ranging from 2.5:1 to 20:1. It was found that the azeotropic mixtures of water and terpene enhanced the separation process and produced a product which was superior in odor and color characteristics. Ninety-five percent pure delta-3-carene can be recovered by the use of a 24 theoretical plate column operated with steam at a reflux ratio of 20:1.

An economic analysis of the process based on the laboratory data indicated that significant return on investment would be obtainable if an adequate market for the delta-3-carene could be developed. At a selling price of \$2.60 per gallon for the 95 percent pure delta-3-carene, a return on investment of 50 percent could be realized.

## INTRODUCTION AND THEORY

The purpose of this project was to examine the availability, the ease of recovery, and the economic feasibility of commercially recovering delta-3-carene from crude sulfate turpentine produced at the Waldorf-Hoerner Paper Products Company pulp mill located in Missoula, Montana.

One of the major problems created by industrial development in this country has been the disposal of objectionable waste products. The disposal of crude sulfate turpentine streams from pulp and paper mills is one of the most striking examples of this problem. The crude turpentine contains a mixture of terpene class chemicals and sulfur compound contaminants which have a high biological oxygen demand. These wastes cause the stream to become sterile and malodorous. It is these properties that complicate the procedures necessary for an acceptable disposal program. After reviewing the methods employed by other industries in overcoming this type of problem, it was felt that a chemical recovery process rather than a waste disposal process would be the most effective approach for arriving at an acceptable solution to this pollution hazard.

In order to evaluate the economic potential of chemical recovery, it was necessary to identify the major components of the crude turpentine stream. This identification was done by qualitative analysis procedures employing the gas chromatograph. Gas chromatography is based on the distribution of the components to be separated between the mobile gaseous stream and the fixed solid packing of the chromatograph column.<sup>5</sup>

A sample of the turpentine is introduced into the carrier gas stream and transported to the column of adsorbant. Since each component of the sample has its own characteristic distribution between the two phases, the components are separated and pass from the column in the effluent stream at different times. By passing the effluent stream through a thermal conductivity detector in combination with an automatic recorder, a convenient, permanent record of the analysis is produced. The qualitative analysis is based on the measure of retention time for each of the components which will be constant under identical operating conditions.<sup>5</sup> Since retention times for the terpene chemicals, which were assumed to be present in the crude turpentine, were not readily available in the literature for the operating conditions to be used in this study, a modified procedure of identification was employed. Pure samples of suspected components were added to the turpentine sample and chromatograms were compared with those of the sample before any additions were made. The enhancement of a peak present in the analysis of the original turpentine was regarded as an indication that that particular terpene was a component of the turpentine. Similarly, the presence of a new peak indicated that the terpene being tested was not a component of the crude turpentine. By this technique it was established that the principal components of the turpentine are alpha-pinene, beta-pinene, delta-3-carene, and dipentene. The structural formula and physical properties of these compounds are given in Table I.

In addition to the identity, the relative amounts of each component are important factors in making an evaluation of the commercial potential of the process. Quantitative analysis by the use of the chromatograph is based on the principle that the area under the peak on a chromatogram is proportional to the amount of substance that produced it.<sup>5</sup> By this method, the turpentine was further characterized as being approximately 40 percent alpha-pinene, 10 percent beta-pinene, 40 percent delta-3-carene, and 10 percent dipentene. Figure 1 is a reproduction of a typical chromatogram of the crude sulfate turpentine from Missoula, Montana. Trace amounts of camphene and an unidentified terpene were also detected in some samples. The unidentified chemical's characteristic peak on the chromatogram could not be satisfactorily resolved from that of dipentene with the adsorbent column used. Since the amount of this chemical present appeared small, the exact identification was not pursued.

From the literature and analyses of other available turpentine samples it was found that the presence of alpha-pinene, beta-pinene, and dipentene in varying amounts is common to most sulfate pulp mill turpentine streams in the United States. However, the delta-3-carene content of the Missoula, Montana turpentine was found to be unique among all those investigated. Table II shows the composition of several crude sulfate turpentine samples. Due to this uniqueness, it was felt that a re-verification of the identity of this component was required. Therefore, infrared analyses of a known sample of delta-3-carene and a sample

of the recovered product were performed and compared. Figures 2 and 3 show reproductions of these analyses which are essentially identical with the exception of the water content responses at three and six micron wave lengths for the known sample. The product sample, having had the water removed with calcium chloride, did not exhibit these responses.

Having established the identity of the delta-3-carene component, the uniqueness of the Missoula, Montana crude sulfate turpentine was suggestive of the potential of a chemical recovery process. Since no source of any magnitude has previously been reported, or exploited, the development of delta-3-carene as an industrial chemical has not been possible. The availability of delta-3-carene is limited even among manufacturers of uncommon or exotic chemicals, thus emphasizing its rarity. Therefore, separation of the chemical fractions by rectification, with special emphasis on the production of high purity delta-3-carene, was studied.

The separation of mixtures by means of fractional distillation and rectification depends upon the difference in composition which usually exists between the boiling liquid and the vapor in equilibrium with it. The process of distillation therefore becomes a series of vaporization and condensation stages in which fractions of similar boiling points are combined and separated from the other fractions, the final enriched vapor being removed at the top of the column. 2,3,6

When the temperature required to vaporize the fraction is near the compound's decomposition temperature, methods must be employed to lower the vaporization temperature. This can be done by lowering the operating pressure of the distillation column or by introducing another component which will form a minimum boiling azeotrope with the fractions to be separated. All liquids can be categorized into five basic classes:<sup>1</sup>

- Class I. Liquids capable of forming three-dimensional networks of strong hydrogen bonds.
- Class II. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms.
- Class III. Liquids composed of molecules containing donor atoms but no active hydrogen atoms.
- Class IV. Liquids composed of molecules containing active hydrogen atoms but no donor atoms.
- Class V. All other liquids.<sup>11</sup>

Steam distillation is an example of azeotropic distillation employing a Class I liquid, water, and a Class V liquid, the terpenes of the crude sulfate turpentine. Since all Class V liquids are very insoluble in water, both substances exert their own vapor pressure, thus forming an azeotrope which will boil at a temperature lower than the normal boiling point of either the water or the terpene.

## RESEARCH OBJECTIVES

The main objectives of this project were to determine the delta-3-carene content of the crude sulfate turpentine from Missoula, Montana, to experimentally set the minimum operating conditions necessary to produce a high purity delta-3-carene product, and to evaluate an economic analysis of the process on an industrial scale.

## EQUIPMENT

The equipment used in this project included distillation columns, Corad condensing heads, stillpots, electric heaters, Powerstats, and a gas chromatograph.

The distillation columns were one-inch diameter glass cylinders of 12, 24, 36, and 48-inch lengths packed with one-eighth inch stainless steel helice packing (Fenske rings) supported on a cone-shaped wire support. The two longer columns employed a set of two concentric glass insulating cylinders of 1.75 and 2.5 inch diameters. The middle cylinder was wound with a Nichrome heating coil to allow adiabatic operation of the column. The two shorter columns used only a single insulating cylinder of 2.5 inch diameter and, therefore, no heating coil. The inner cylinder was wrapped with aluminum foil in order to reduce the heat loss from the shorter columns. Ground glass joints at each end of the inner cylinder provided leak-free connections with the stillpot and condensing head.

The Corad condensing heads used permitted operation of the column at reflux ratios of 2.5:1, 5:1, 10:1, 20:1, and 30:1.

One- and two-liter flasks were employed as stillpots. The stillpot was heated with a 550-watt electric resistance heater controlled by a 0-140 volt variable Powerstat. A similar Powerstat was used to control the output of the Nichrome heating coil on the larger columns.

The compositions of the various feed and product samples were analyzed by means of a Wilkens Instrument and Research Company Aerograph gas chromatograph. This instrument was fitted with a one-fourth inch stainless steel tube, six feet long, packed with Carbowax 4000 adsorbent on Chromosorb C-48560 supports.<sup>7</sup> A Minneapolis-Honeywell recorder was used with the chromatograph.

A compensating polar planimeter was used to evaluate the characteristic peak areas produced by the chromatographic analysis.

An equipment diagram is shown in Figure 4.

## EXPERIMENTAL PROCEDURE

Samples of the crude sulfate turpentine streams from several pulp mills were analyzed by means of the gas chromatograph. Two micro-liters of the sample were injected into a stream of helium gas flowing at approximately 50 milliliters per minute, which transported it to the column adsorbent packing of Carbowax 4000. The chromatograph was operated at 80°C and the thermal conductivity detector filament carried a current of 190 milli-amperes. The raw turpentine used as feed and the product streams were similarly analyzed by gas chromatography. The turpentine samples were obtained from Missoula, Montana in order to represent the stream over a period of approximately one year. Special emphasis on the stream composition over a two-month period was obtained by the analysis of weekly samples.

In an effort to determine the minimum conditions required for the production of high purity delta-3-carene, distillation runs were made with columns of 6, 12, 18, and 24 theoretical plates at reflux ratio settings on a Corad condensing head ranging from 2.5:1 to 20:1. An initial charge of 500 milliliters of crude sulfate turpentine was introduced into the stillpot and heat applied until the delta-3-carene fraction had passed through the column. When steam distillation was used, 750 milliliters of water were also added to the stillpot before the run was started. The overhead was recovered from the steam distillation in two phases and separated by decantation. The terpene-to-water ratio in the overhead was about one to one on a volume basis.

The first 200 milliliters of terpene overhead contained primarily alpha-pinene, the next 100 milliliters a relatively equal mixture of beta-pinene and delta-3-carene, and the third fraction was 100 milliliters of high purity delta-3-carene. The stillpot residue was a mixture of delta-3-carene and dipentene. Samples of approximately 20 milliliters each were taken throughout each distillation run and analyzed by means of the gas chromatograph.

Distillation runs made with the six theoretical plate column proved to be of no utility with regard to the production of a high purity product. Although the 12 theoretical plate column was ineffective for actual product recovery, it was found to be sufficient for making an initial separation in which the alpha-pinene fraction was taken from the crude turpentine charge. This topping column was operated at a reflux ratio of 5:1 and its use facilitated a significant reduction in the required size of the precision column due to the reduced throughput.

The area under the peaks produced by the chromatographic analysis was considered to be proportional to the relative amounts of the substances producing the peaks. For very accurate quantitative analysis this method must be modified by correction factors based upon the molecular weight and class of compound. Since all components of the samples analyzed in this work were of the terpene chemical class and all had the same molecular weight, these correction factors were not included.

Additionally, when internal normalization of the peak areas is used in order to provide the relative distribution of the components rather than an exact quantitative analysis, these correction factors are of less importance.

A number of methods have been proposed for measuring the peak area:<sup>5</sup>

1. Cut out the peak with a scissors and weigh the paper.
2. Measure the area with a planimeter.
3. Multiply the peak height by the peak width at half the peak height.
4. Multiply the peak height by the retention time.
5. Use an automatic integrator.

Since the characteristic peak for dipentene was not completely symmetrical under the operating conditions used in the chromatograph, multiplication of the peak height by either the peak width at half the peak height, or retention time was not suitable for this analysis. An automatic integrator was not available. Therefore, measurement of the peak areas by means of a planimeter was chosen since its single operation was felt to be more accurate than cutting out the peaks with a scissors and weighing the paper.

Results of the distillation runs are shown in Figures 5 and 6. These results correlate the purities obtainable in this study with various degrees of recovery. Since the purity decreases with recovery,

an effort was made to find an optimum relationship between the two. From these results it appears that the incremental decrease in purity is much greater at recoveries above 50 percent. Therefore, it is felt that 50 percent recovery is the maximum obtainable in order to preserve the high purity requirements.

## ECONOMIC ANALYSIS

In order to evaluate effectively the commercial potential of this project, an economic analysis of the process based on the laboratory data obtained was completed. Because of the previous lack of a sizeable quantity source that would stimulate industrial interest, delta-3-carene is an undeveloped chemical as far as commercial application is concerned. Therefore, no indication of selling price was available upon which to base an economic study. This analysis has provided a correlation between selling price, return on investment, and purity.

As in all economic studies, certain costs must be estimated since exact figures are not available until the equipment is actually installed and the plant is operating. In this analysis it was attempted to estimate these costs at their maximum value in order to provide a conservative figure for return on investment. Some of these estimations are:

1. Total installed equipment cost = 2.5 times material cost of equipment
2. Auxiliary equipment = 30 percent of total installed equipment cost
3. Land and building cost = \$12,000
4. Utilities cost = \$1,000 per year
5. Labor cost = \$800 per week

Other cost figures are developed from quotes on the various items of equipment as furnished by several manufacturers. It is realized that these quotes may be high or low when compared to isolated markets for

a specific piece of equipment, but they are felt to be representative averages upon which the overall analysis can be based. Among the manufacturers whose quotes are used in this study are:

1. Artisan Industries, Inc., Waltham, Massachusetts
2. Matt. Corcoran Company, Louisville, Kentucky
3. Pacific Hide & Fur Company, Bozeman, Montana
4. Perry Equipment Corporation, Philadelphia, Pennsylvania
5. Struthers Wells Corporation, Warren, Pennsylvania

This analysis is based on a production of 1000 gallons per day of the crude turpentine, available at \$0.13 per gallon, which are the figures estimated by Waldorf-Hoerner. The process will be batch distillation with two forty-hour runs per week. The crude turpentine contains 40 percent delta-3-carene. From laboratory data it was found that a recovery of 50 percent of the delta-3-carene is the maximum allowable in order to preserve the high purity under the operating conditions investigated. Similarly, it is apparent that the operation of two columns, one a smaller column functioning as a topping column in which the alpha-pinene fraction is removed and the other a precision column where a more complete separation of the remaining fractions is accomplished, is the optimum procedure.

A flow diagram for this process is given in Figure 7.

Column Requirements (sample calculations)

From laboratory data:

Number of theoretical plates = 12  
 Reflux ratio = 5:1  
 Atmospheric distillation

From literature:

Plate efficiency for terpene system based on  
 viscosity correlations = 75 percent

$$\text{Maximum vapor velocity} = 0.15 \sqrt{\frac{P_L - P_V}{P_V} h}$$

where

 $P_L$  = Liquid density, lb/cu ft $P_V$  = Vapor density, lb/cu ft

h = Tray spacing, ft

$$\begin{aligned} \text{Number of actual plates} &= \frac{\text{Number of theoretical plates}}{\text{Plate efficiency}} \\ &= \frac{12}{0.75} = 16 \text{ Plates} \end{aligned}$$

$$\text{Throughput} = (\text{Production})(\text{Reflux ratio} + 1)$$

$$\begin{aligned} &= \frac{(1400 \text{ gallons})(7.33 \text{ lbs/gallon})(5 + 1)}{(40 \text{ hours})(0.2 \text{ lbs/cu ft})(3600 \text{ sec/hour})} \\ &= 2.13 \text{ cu ft/sec} \end{aligned}$$

$$\begin{aligned} \text{Maximum vapor velocity} &= 0.15 \sqrt{\frac{54.8 - 0.2}{0.2}} 1.5 \\ &= 3.03 \text{ ft/sec} \end{aligned}$$

$$\begin{aligned} \text{Column area} &= \frac{\text{Throughput}}{\text{Maximum vapor velocity}} \\ &= \frac{2.13 \text{ cu ft/sec}}{3.03 \text{ ft/sec}} = 0.70 \text{ sq ft} \end{aligned}$$































































