MONTANA STATE UNIVERSITY

Recovery of alpha-pinene and delta-3-carene from crude sulphate turpentine
by Eugene Bruce Greene

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:
This investigation was performed to determine the method of operation necessary to recover high purity terpene chemicals from crude sulfate turpentine. The terpenes to be recovered were alpha-pinene and delta-3-carene and the purity was 95% for each of the compounds.

The separation of alpha-pinene and delta-3-carene from the turpentine produced by Waldorf-Roerner Paper Products Company of Missoula, Montana was performed in distillation columns of 24, 36 and 45 theoretical plates. Only the 45 theoretical plate column resulted in good recovery of both the alpha-pihene and the Delta-3-carene.

The best distillation system was found to be a batch-steam distillation system, operating with a variable 'reflux ratio and a 45 theoretical plate column. With this system the average recovery of the available alpha-pinene is 80% and the average recovery of the available delta-3-carene is 30%.

An economic analysis was performed on the average composition of the feed available from Waldorf-Hoerner. When 7000 gallons of turpentine are processed per week, there is an initial investment of $251,000, a. return on investment of 32% and a payout time of 2.37 years.

RECOVERY OF ALPHA-PINENE AND DELTA-3-CARENE

FROM CRUDE SULFATE TURPENTINE

by

EUGENE BRUCE GREENE

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

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in

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Approved:

Lloyd Berg

Head, Major Department

Lloyd Berg

Chairman, Examining Committee

Norris D. Smith

Dean, Graduate Division

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ABSTRACT

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INTRODUCTION

Since the turn of the twentieth century the United States has become primarily an industrial country. Along with industrialization come some of the objectionable factors such as air and water pollution. Air and water pollution is the result of exiting waste streams directly into the atmosphere and water bodies without proper treating.

Recently, various communities and states have established laws requiring the treating of waste streams. Industry has found that the waste streams which contain some potentially valuable chemicals often make the treating a profitable operation rather than an expense.

One of the worst industries for air and water pollution is the pulp and paper industry. One of their pollution problems is the disposal of the crude sulfate turpentine. This crude turpentine, a byproduct of the digesters, has a very pungent odor. If the crude turpentine is vented to the atmosphere, the odor places a hardship on the community-company relationship. If the crude turpentine is dumped into the water bodies, the sulfur compounds contained in the turpentine have such a high biological oxygen demand that the water becomes sterile.

The waste crude sulfate turpentine is easily treated to be of commercial grade turpentine. The market for turpentine, however, has stabilized and is not dynamic. On the other hand, the market for pure terpene chemicals is increasing (2).

The reason the pure terpenes are increasing in demand is their use as intermediates in the synthesis of camphor, terpene resins, insecticides and many other products (2).

All crude sulfate turpentines contain alpha-pinene, beta-pinene, camphene and dipentene. There are additional terpenes in the crude turpentine depending upon the type of tree being pulped and the location of the trees geographically (3).

The Montana source of crude sulfate turpentine (Waldorf-Hoerner Paper Products Company, Missoula, Montana) contains alpha-pinene, beta-pinene, camphene, dipentene and delta-3-carene. The delta-3-carene is a rare chemical found only in the sulfate liquor from western pondorosa pine (3). H. T. McCumber (4) analyzed the turpentines of many of the pulping companies located in the western part of the United States. The results of these analyses indicate that the trees must grow in a relatively dry climate if delta-3-carene is to be present.

The crude turpentine output from the Waldorf-Hoerner Company was analyzed periodically from March, 1962 to April, 1963 (4). These analyses showed that the composition of the turpentine was fairly variable. The main variations occurred in the alpha-pinene and delta-3-carene content. The amount of these two terpenes varied from 27.8% to 45.5% by weight for the alpha-pinene and from 28.7% to

50.3% by weight for the delta-3-carene. Analysis of a later sample
(June, 1964) showed that these ranges may sometimes be larger. The
alpha-pinene and delta-3-carene contents of this sample were 20.5%
and 63.2% respectively.

The percentage of the beta-pinene and dipentene is 10% ± 2.5%
and only trace amounts of camphene. The structural formulae and
physical properties are given in Table VIII.

In the December 23, 1963 issue of Chemical and Engineering News
an article announcing that delta-3-carene could be made available for
industrial use was published (5). Because of the large number of
requests for samples, one hundred and seventy-five, it became
evident that more information regarding the separation of the terpenes
in the Waldorf-Hoerner turpentine was needed before a commercial plant
could be established to produce high purity terpenes.

The possible methods of separating the terpenes are: distilla-
tion, solvent extraction, and crystallization. Fractional distilla-
tion is most favorable economically if the desired separation can be
accomplished without going to too much expense for the distillation
column and the heating requirements.

Fractional distillation as a method of separating mixtures depends
upon the difference in composition between a boiling liquid and the

vapor leaving the liquid. The distillation process becomes a series of vaporization and condensation stages with the more volatile component being removed at the top of the column.

There are two general types of distillation processes (continuous distillation and batch distillation) and several subdivisions. The most common of the subdivisions are:

1) atmospheric distillation

2) vacuum distillation

3) azeotropic distillation

When the boiling point of a chemical compound is near the decomposition temperature, means must be taken to reduce the boiling point. This can be done by either azeotropic distillation or vacuum distillation.

Azeotropic distillation is the introduction of another component which will form a minimum boiling azeotrope with the compound to be separated. Steam distillation on terpenes is a special form of azeotropic distillation employing Class I and V liquids (1). This form of azeotropic distillation is an immiscible system of water (Class I) and the insoluble terpenes (Class V). In this type of system each phase will exert its own vapor pressure and boiling will take place when the sum of the two vapor pressures is equal to the total pressure. Of course, this will be at a temperature which is less than the normal

boiling point of either phase.

Steam distillation is needed in the separation of the terpenes because:

1) the decomposition temperature of the terpenes is near their normal boiling point.

2) a better separation can be achieved for a given distillation column.

3) the product produced by steam distillation is much more pleasant smelling and clear in color (4).

When large amounts of material are to be processed or the process is well defined, continuous distillation is more economical to operate than batch distillation. The terpenes available for processing are relatively small in amount and the process to separate them is not well defined. This leads to the conclusion that initially a batch distillation system must be used.

Within the batch distillation system there are two general methods of operation. Method 1 is to operate at a set reflux ratio over the entire distillation range. Method 2 is to change the reflux ratio when the purity deviates below a set standard (6).

Method 1 with the set reflux ratio is easier to operate than Method 2. Method 1 is also desirable when the reflux ratio and number

of theoretical plates required for the separation is never very high.

Method 2 with the variable reflux ratio is desirable when the number of theoretical plates and reflux ratio is in the precision separation range, i.e. theoretical plates greater than 25 and reflux ratio greater than 10:1. However, there are objections to the variable reflux ratio process. The process is harder to control since the operation is not only operating unsteady from the standpoint of the changing still pot composition but allowances must be made for the change in reflux ratio as the overhead is taken off.

In a multicomponent batch distillation system where there are no azeotropes formed, the distillation process is a series of binary separations. For the Waldorf-Hoerner turpentine the sequence of binary separations would be alpha-pinene from camphene, camphene from beta-pinene, beta-pinene from delta-3-carene and delta-3-carene from dipentene. Due to the small amount of camphene present in the turpentine the binary separations of alpha-pinene from camphene and camphene from beta-pinene can be reduced to one binary separation of alpha-pinene from beta-pinene.

For the removal of high purity alpha-pinene, the binary which must be studies is the alpha-pinene beta-pinene binary system.

For the removal of high purity delta-3-carene there are two binaries involved. These binaries are the beta-pinene delta-3-carene binary and the delta-3-carene dipentene binary. Since the beta-pinene delta-3-carene binary has previously been studied, only the delta-3-carene dipentene binary must be defined (7).

As was mentioned previously, the amount of the alpha-pinene and delta-3-carene in the crude turpentine is highly variable. Therefore, to define the separation of these terpenes from the crude turpentine, the binary compositions in the still pot at the time the overhead product is just at the standard purity must be known. This limiting binary composition must be known since it is not a function of the feed stock. The limiting binary composition will only be a function of the number of theoretical plates and reflux ratio used.

RESEARCH OBJECTIVES

The objectives of this project were to determine the method of
operation necessary to produce alpha-pinene and delta-3-carene in
purity of 95 per cent from commercial grade waste sulfate pulp liquor
and to evaluate an economic analysis of the process.

EQUIPMENT

The equipment used in the project included distillation columns, mantle heaters, still pots, Corad condensing head, Variacs, a gas chromatograph and compensating polar planimeter.

The distillation columns were one inch diameter glass columns wrapped with Nichrome heating wire with a 2 1/2 inch diameter glass jacket.

The heights of the columns were 46 inches and 36 inches packed with one-eighth inch stainless steel Fenske rings and a short 24 inch column packed with three-sixteenth inch stainless steel Fenske rings. The number of theoretical plates for these columns were 24, 21 and 12 respectively. Thus by stacking them into a 70 inch column, 36 theoretical plates were obtained and in the 82 inch column 45 theoretical plates were obtained.

The Corad condensing head was a variable reflux condensing head with reflux ratios of 2.5:1, 5:1, 10:1, 20:1 and 30:1 available.

The gas chromatograph used for analytical purposes was a Wilkens Instrument and Research Company Aerograph model A-110-C. This instrument was fitted with a 1/4 inch stainless steel tube seven feet long packed with Ucon Polar 50 HBJ 100 absorbent on Chromosorb P. 35/80 mesh support. A Minneapolis Honeywell recorder was used in conjunction with the chromatograph.

The compensating polar planimeter was used for measuring the characteristic peak area produced by the chromatograph.

TEST PROCEDURE

Operation of the Gas Chromatograph

The gas chromatograph was an Aerograph Model A-110-C equipped
with a 1/4 inch stainless steel tube seven feet long. This tube
was packed with Ucon Polar 50HBJ100 absorbent on Chromosorb P 35/80
mesh support.

The chromatograph was operated at a temperature of 105° C. with
helium carrier gas flowing at a rate of 45 to 60 milliliters per
minute. The thermal conductivity detector filament carried a current
of 200 milli-amperes.

These conditions resulted in retention times of 7 minutes
for the alpha-pinene, 9 minutes for the camphene, 12 minutes for
the beta-pinene, 14 minutes for the delta-3-carene and 18 minutes
for the dipentene.

The separation of these components was good as even at a high
purity of one component there was at least one-quarter of a minute
in which the recorder followed the base line.

Because of the high degree of purity set for the alpha-pinene
and delta-3-carene (95% pure), a method of analyzing the samples
was needed. The problem was that when operating the gas chromato-
graph at a sensitivity which would keep the large peak on the

recording paper, the lesser pure constituents would barely show up

on the recording paper making analysis difficult and error a problem.

The procedure to obtain an accurate measure of the purity was to

operate the chromatograph at a sensitivity such that the large peak

would stay on the recording paper, and for the impurity components

the sensitivity was changed to four times the sensitivity of the pure

component. In this manner of testing, the experimental error in

measuring the area under the small peaks was divided by a factor of

four.

Determination of the Still Pot and Binary Compositions

Initially, one thousand milliliters of turpentine and one

thousand milliliters of water were charged to the still pot. After

the column had been flooded, the Variacs were turned to a setting

slightly below flooding velocity. The column was allowed one half

hour to come to equilibrium. The reflux ratio was set and overhead

product was continuously drawn off. The product was collected in a

water cooled, graduated separatory flask so the volume of the overhead

product was known at all times during the run. Instantaneous overhead

samples were taken at approximately every 5% by volume of the original

charge distilled off. These samples were analyzed by injecting two

microliters into the chromatograph and measuring the areas under the

curves with the compensating polar planimeter. When the purity of the

instantaneous overhead product became 95% pure of one component the

column was shut off and the cumulative overhead product was analyzed to determine its composition.

The determination of the still pot composition then became a material balance on the terpenes. By knowing the amount and composition of the overhead product and also the amount and composition of the feed, then by subtracting the overhead product from the feed, the still pot composition was determined. From the still pot composition, the necessary binary composition was determined.

After recharging the still pot, by going through the same procedure except for selecting a new reflux ratio, the still pot composition at various reflux ratios for the column was determined and thus, the binary composition for the various reflux ratios.

Obtaining the Delta-3-Carene-Dipentene Binary

To obtain the delta-3-carene-dipentene binary, the losses of delta-3-carene in the alpha-pinene-beta-pinene-delta-3-carene mid-fraction were minimized by operating at a high reflux ratio. The reflux ratio used was a 20:1 since this was the last reflux ratio used in the determination of the alpha-pinene removal.

When the instantaneous overhead product became 95% pure delta-3-carene, the mid-fraction separation was considered complete and the reflux ratio was set for the removal of the delta-3-carene.

RESULTS AND DISCUSSION

When operating a multicomponent batch distillation column in
which the feed composition is variable, it is necessary to know the
binary composition in the still pot when the overhead is at the
standard. For the removal of alpha-pinene, it is necessary to know
the composition of the alpha-pinene beta-pinene binary in the still
pot at the various reflux ratios. The binary for the delta-3-carene
removal is the delta-3-carene-dipentene binary.

These binary compositions in the still pot for reflux ratios
of 2.5:1, 5:1, 10:1 and 20:1 and columns with theoretical plates
of 24, 36 and 45 are listed on Table VII page 34.

These values were calculated by applying a material balance on
the feed and overhead product. This method of calculation neglects
the hold-up in the column which was one (1) milliliter per cubic inch
of packing. With a feed of 1000 milliliters this hold-up becomes quite
considerable (as much as 3.2% of the feed charge) and must be accounted
for. To account for this hold-up, the following assumptions were made.

1) The hold-up is 50% water and 50% terpenes by volume.

2) The composition of the terpenes in the column is 50% by
weight of the more volatile component.

3) The composition of the material in the still pot changes only
as a result of removal of the more volatile component.

Using these assumptions the adjusted still pot binary compositions were calculated. The adjusted values are also presented on Table VII .

The adjusted values for the binary compositions contain a factor of safety as the assumption that the composition in the column is 50% by weight of the more volatile component is not exactly correct. The actual composition should be more than 50% more volatile component.

It should be noted that for the 24 theoretical plate column no binary compositions for the delta-3-carene removal were made. The reason for this was that a graph of reflux ratio versus per cent alpha-pinene removed indicated more theoretical plates were needed in the alpha-pinene recovery before a substantial amount of high purity alpha-pinene could be removed.

For purposes of a plant design the adjusted binary compositions were used to calculate a theoretical graph of reflux ratio versus per cent distilled for the average turpentine composition which is 40% alpha-pinene, 40% delta-3-carene, 10% beta-pinene 10% dipentene by weight and trace amounts of camphene and heavy oils. The purpose of this type of graph is to determine the average reflux ratio for the entire distillation cycle. Since the feed will be variable, the recovery of delta-3-carene and alpha-pinene will vary with each batch. However, for an extensive period of time the recovery should be that

obtained with a feed of the average composition. Also when the concentration of alpha-pinene is low the concentration of delta-3-carene is high. This means that when the starting reflux ratio for the delta-3-carene removal is lowered and the average reflux ratio for any given batch of material should be close to the average reflux ratio of the average composition.

The average reflux ratio for the distillation of the average feed was calculated to be 13.8:1 for the 36 theoretical plate column and 12.6:1 for the 45 theoretical plate column. However, the 36 theoretical plate column would have rather limited usage as the recovery of the delta-3-carene would be very low, only about 20% of the available delta-3-carene. The additional nine (9) theoretical plates increases the recovery of delta-3-carene from 20% recovery to 30% recovery and with the reduced average reflux ratio, the cross sectional area of the column, condensers and heating requirements would be reduced. The increase in recovery of delta-3-carene can be seen by comparing Figures 1 and 2, pages 36 and 37.

The mid-fraction, i.e. the material removed as overhead in going from 95% pure alpha-pinene to 95% pure delta-3-carene, will consist of beta-pinene, alpha-pinene and delta-3-carene. This fraction amounts to 30% of the feed charge and will also have a variable composition. However, experimental results indicate that the composition of this mid-fraction will be 30% ± 3% for each of the three major constituents.

This analysis appears to hold true, for both the 36 theoretical plate column and the 45 theoretical plate column when operated at a reflux ratio of 20:1. The distillation curves for the mid-fraction are presented on Figures 3 and 4. It should be noted that the higher instantaneous purity for the beta-pinene was obtained in the 36 theoretical plate column rather than the 45 theoretical plate column because the ratio of beta-pinene to delta-3-carene in the feed stock was much higher for the runs made with the 36 theoretical plate column. This was the result of a depletion of original feed stock and obtaining more at a later date. The effect of changing the ratio of beta-pinene to delta-3-carene in the feed stock from 0.19 to 0.12 decreased the instantaneous purity of beta-pinene from 59% to 40% when operating with the 36 theoretical plate column.

The operational method by which high purity alpha-pinene and delta-3-carene can be removed from Waldorf-Hoerner turpentine can be summarized by the following steps.

1) Analyze feed with gas chromatograph.

2) Determine the starting reflux ratio by calculating the ratio of alpha-pinene to beta-pinene in the feed and locating where this ratio is on the adjusted values of Table .

3) Determine how much material can be removed at the starting reflux ratio before changing to a higher reflux ratio by

assuming no beta-pinene will be removed as overhead and using

the binary composition of Table VII again.

4) Continue with this procedure for succeeding reflux ratio

changes.

This method of operation is only good for a distillation column

operating with no hold-up. If the ratio of hold-up to feed is small

then the effect of hold-up can be neglected.

PLANT DESIGN

After reviewing Figures 1 and 2, it is obvious that a plant design should be based upon the 45 theoretical plate column. This then would be a variable reflux ratio, steam distillation system with 45 theoretical plates.

With the column thus defined, all other sizing calculations are based upon how fast each batch of feed must be processed and how large each batch of feed will be. Waldorf-Hoerner estimates the volume of terpenes available for processing at 1000 gallons per day or 7000 gallons per week. Looking ahead to the work force requirements, there would be a need for four operators, one maintenance employee and one supervisor-engineer. To allow these employees to receive a full work week of 40 hours it appears that the scheduling of two batches per week with a throughput time of forty hours per batch meets the conditions satisfactorily.

With the forty hours as total distillation time, the 3500 gallons as charge and Figure 2 giving the per cent of charge to be distilled, 75%, the throughput then becomes:

$$\text{Throughput} = (\text{Terpene Throughput} + \text{Water Throughput})(R+1)$$

$$\text{Throughput} = \left[\frac{(0.75)(3500 \text{ gal.})(7.33 \text{ lbs./gal.})}{(40 \text{ hrs.})(0.2 \text{ lbs/cu. ft.})(3600 \text{ sec/hr.})} \right.$$
$$\left. + \frac{(0.75)(3500 \text{ gal.})(8.33 \text{ lbs/gal.})}{(40 \text{ hrs.})(0.027 \text{ lbs/cu. ft.})(3600 \text{ sec/hr})} \right] (R+1)$$

Throughput = 6.28 $(\bar{R} + 1)$ cu. ft./sec.

since $\bar{R} = 12.6:1$

Throughput = 85.4 cu ft./sec.

The maximum vapor velocity was found from literature to follow the equation:

$$\text{Maximum Vapor Velocity} = 0.15 \left[\frac{D_1 - D_v}{D_v} H \right]^{1/2}$$

where D_1 is liquid density lbs/cu ft $= \dfrac{54.8 + 62.4}{2}$

$= 58.6$ lbs/cu ft.

D_v is vapor density lbs/cu ft

$= \dfrac{0.2 + 0.027}{2} = 0.114$ lbs/cu ft.

H is plate spacing $= 1.5$ ft.

Operating at 80% of maximum vapor velocity, the operating velocity becomes:

$$\text{Operating Velocity} = (0.80)(0.15) \left[\frac{(58.6 - 0.114)(1.5)}{(0.114)} \right]^{1/2}$$

$= 3.34$ ft/sec

From the throughput and vapor velocity the column cross sectional area can be found to be:

$$\text{Area} = \frac{85.4 \text{ cu ft/sec}}{3.34 \text{ ft/sec}} = 25.5 \text{ sq ft}$$

or a plate diameter of 69 inches.

The correlations available of theoretical plates to actual plates indicate an actual plate efficiency of 90% for the terpene-water system. To be on the conservative side an efficiency of 75% was used and the number of actual plates required for the separation would be 60 plates.

The column is now sized to be 60 plates, 69 inches in diameter with plate spacing of 1.5 feet.

In sizing the condensers the condensing system must be defined. The system is a shell and tube heat exchanger located at the top of the column to remove the latent heat of vaporization and another heat exchanger located on the ground to remove 80 Fahrenheit degrees of sensible heat. The heat exchanger at the top of the column will be mounted vertical so the cross section of the tubes is in line with the column cross section. In this manner the rising vapor will condense inside the tube and the liquid will flow down the tube and drop to the plate below. The desired reflux ratio can be obtained by removing the down coming liquid from the same ratio of tubes. Through slight modifications any number of reflux ratios can be built into the top condenser. The following data is needed before the areas of these two condensors can be found:

Heat of Vaporization of Terpenes   68.6 BTU/lb.

Heat Capacity of Terpenes   0.4 BTU/lb .°F

Heat of Vaporization of Water   970 BTU/lb.

Heat Capacity of Water   1 BTU/lb °F

Overall Heat Transfer Coefficient for Condensing

$$150 \text{ BTU}/ \text{ ft}^2 \text{ hr } °F$$

Overall Heat Transfer Coefficient for Cooling

$$115 \text{ BTU}/ \text{ hr ft}^2 °F$$

Assume water available at 40 °F and will exit at 80 °F

With the above data and assumptions, the heat duty for the two heat exchangers is:

Condensing: $\dfrac{13.6(0.75)(3500)}{40} \left[(7.33)(68.6) + (8.33)(970) \right]$

$$= 10,600,000 \text{ BTU/hr}.$$

Cooling $\dfrac{(0.75)(3500)(80)}{40} \left[(7.33)(0.4) + (8.33)(1) \right]$

$$= 59,200 \text{ BTU/hr}$$

The required area for the condenser follows the equation:

$$q = -UA \, \Delta T_{\text{ln mean}}$$

Therefore the area for condensing is:

$$A = \dfrac{-10,600,000}{150 \left[\dfrac{(195-80) + (195-40)}{2} \right]} = 543 \text{ ft}^2$$

The area for cooling is:

$$A = \dfrac{-59,200}{-115 \left[\dfrac{(195 - 80) \quad (105 - 40)}{2} \right]} = 6.5 \text{ ft}^2$$

We now have the two heat exchangers sized to be 543 ft^2 for condensing and 6.5 ft^2 for cooling.

When operating with steam distillation, there is no need for a heating element on the reboiler as steam can be charged directly to the terpenes. In this manner of operation only a steam sparger would be needed to disperse the steam in the terpene phase.

The auxiliary equipment that is needed in the terpene separation can best be presented by listing the specialty equipment rather than the standard. The specialty equipment is;

1) one gas chromatograph

2) one recorder with built-in integrator

3) two flow meters

4) generally, no rubber, polypropylene, poly-ethylene or neoprene gaskets where the terpenes will come in contact with gaskets or hoses. At the present time it has been found that only "Teflon" will withstand the solvent properties of the terpenes.

A one week storage should be adequate for both the finished products and the crude liquor. There would be storage tanks for: crude turpentine, alpha-pinene, beta-pinene mid-fraction, delta-3-carene and the dipentene-rich fraction (bottoms). Once again using Figure 2 as the basis for calculations, the storage of these products will require a 7000 gallon capacity for crude turpentine, 2200 gallons for alpha-pinene, 2000 gallons for beta-pinene mid-fraction, 1050 gallons for delta-3-carene and 1750 gallons for dipentene fraction. Since

storage tanks do not come in odd sizes, the actual storage tank sizes would be 10,000 gallon tank for crude and 5000 gallon tanks for each of the products. This results in slightly more than a two week storage capacity for the finished products.

The reboiler would necessarily be 3500 gallon capacity. Again allowing an overdesign and the use of standard sizes, the reboiler would be a 5000 gallon tank.

All the major equipment has now been sized. Using the standard sizes furnished by manufacturers the specifications for the equipment are:

Table I: Standard Equipment Specifications

Description of Equipment	Calculated Size	Standard Size	Company	Price
Column	60 Plates	72 in. Diameter	Matt Corcoran Co.	$864/Plate
Overhead Condensor	543 ft^2	662 ft^2 Designed for Vertical Condensing 18N12	Struther Wells Corp.	$2380
Cooling Condensor	6.5 ft^2	20 ft^2 6N4	Struther Wells Corp.	$500
Kettles	(1) 10000 gal. (5) 5000 gal.		Pacific Hide and Fur Co.	$2000 $1200

Now that the major equipment has been priced and sized, there is a need for the job description and a production schedule so a rate of pay can be established and also an economic analysis of the process. The job description and production schedule are tabulated below.

Table II: Job Description

Job	Number of Employees	Duties	Hours Employee Works per week
Maintenance	1	Empty and Refill reboiler twice a week Cleaning of Column Once a Week General Maintenance	40
Operating Employees	4	Perform Necessary Changes in Operation Fill Orders Minor Maintenance	40
Supervisor-Engineer	1	Analyze Feed Calculate Positions for Change in Reflux Ratio General Management Look for New Outlets for Products	40

Table III: Production Schedule

Time	Monday	Tuesday	Wednesday	Thursday	Friday
12 PM to 8 AM	Fill Reboiler Start Heat-up	Distillation		Fill Reboiler Start Heat-up	Distillation
8 AM to 4 PM	Distillation	Distillation		Distillation	Distillation
4 PM to 12 PM	Distillation	Distillation and Shut Down		Distillation	Distillation and Shut Down

The maintenance employee would work from 12 P.M. to 8 A.M. five days a week. The supervisor-engineer would work from 8 A.M. to 4 P.M. five days a week. The two operating crews with two operators on each crew would alternate the distillation shifts and would work 5 eight hour shifts each week.

The established rate of pay in Missoula, Montana for employees with the above-mentioned skills except for the supervisor-engineer appears to be $2.25 per hour. However, because of the peculiar hours to be kept by this type of operation and as an incentive to work, the rate of pay should be increased to $2.50 per hour. The supervisor-engineer would receive $8400 per year.

It should be noted that with this production schedule there is the advantage of possible expansion to a three batch per week production schedule by adding one more operating crew and working a six day week.

It is now obvious that an economic analysis must be performed to determine whether the previously described process is feasible. Whenever an economic analysis is performed there are a few assumptions that are used. Some of the assumption to be used in this economic analysis are:

Installed Equipment	2.5 times Equipment Cost
Auxiliary Equipment	30% of Installed Equipment
Working Capital	3 months Expenses
Labor Benefits	25% of Labor Costs

Summing the various capital expenses of Table I results in a total major equipment cost of $62,880. Applying the first assumption listed above, the installed equipment cost is $157,000.

Waldorf-Hoerner Paper Products Company estimated the price of the crude turpentine at $0.13 per gallon. They also have available low pressure steam at an estimated cost of 25 cents per thousand pounds. If the installed equipment is depreciated on the straight-line method over a period of ten years, maintenance is estimated at ten per cent of installed equipment cost and taxes and insurance estimated at three per cent of installed equipment cost, then the cost of the operation per week can be found. These costs are tabulated as follows:

Table IV: Operating Costs Per Week

Item	Cost per Week
Steam, Raw Materials and Utilities	$1200
Wages and Benefits	825
Depreciation	303
Taxes and Insurance	90
Maintenance	303
Total	$2721

The total initial investment is obtained by summing the installed equipment, auxiliary equipment, land and building, and working capital.

The land and building is estimated as $7.50 per square foot for 1600 square feet of building. Auxiliary equipment is 30% of installed equipment cost and working capital is three months expenses. The various items totaling the initial investment are tabulated below.

Table V: Initial Investment

Item	Cost
Total Installed Equipment Cost	$157,000
Auxiliary Equipment	47,000
Land and Building	12,000
Working Capital	35,000
Total Initial Investment	$251,000

The revenue obtained by selling the pure terpenes will be 30 cents per gallon for the alpha-pinene, 40 cents per gallon for the beta-pinene mid-fraction, 5.00 dollars per gallon for the delta-3-carene and 10 cents per gallon for the dipentene rich fraction. The only price which is actually quoted is the alpha-pinene price. The beta-pinene mid-fraction price is an estimated interplant price for a process which separates the beta-pinene into a high purity product with by-products of alpha-pinene and delta-3-carene. The price for the delta-3-carene is a suggested market price, at least for initial production. The price for the dipentene rich fraction is a fuel value price.

Using the average composition of Figure 2 for the amount of each material to be produced and the above selling prices, the revenue then becomes:

alpha-pinene	$ 31,400
beta-pinene	43,700
delta-3-carene	236,000
dipentene	9,100
Total annual revenue	$320,000

Using the results of Table IV and V, the revenue figure from a-bove and assuming Federal and State taxes are 55%, then the return on investment and payout time can be found. These values are tabulated below.

Table VI: Return on Investment and Payout Time

Item	Amount
Initial Investment	$251,000
Revenue	320,000
Expenses Including Depreciation	141,000
Taxes	98,500
Net Income	80,700
Depreciation	25,100
Return on Investment	32%
Payout Time	2.37 years

This economic analysis and plant design was performed in a conservative manner. The return on investment of 32% and the payout time of 2.37 years indicate that the terpene separation can be performed economically. The only hinderance to the proposed design is in establishing an initial stable market for the delta-3-carene.

CONCLUSIONS

The removal of alpha-pinene and delta-3-carene in purities
of 95% from the crude turpentine produced by Waldorf-Hoerner
Paper Products Company of Missoula, Montana is a difficult separa-
tion. However, the separation can be accomplished in a 45 theoretical
plate distillation column operating with a variable reflux ratio and
steam distillation.

An economical evaluation of the distillation system shows a
return on investment of 32% and a payout time of 2.37 years.

SUGGESTIONS FOR FUTURE STUDY

Since the process of terpene separation depends, economically, upon the marketing of delta-3-carene, there is a need to get high purity test samples to industrial companies. These companies may be able to find a use for the delta-3-carene.

The reaction kinetics could also be studied on the hydrogenation of alpha-pinene to pinane.

Another area where research is needed is in the separation of dipentene from the other heavy oils. If dipentene could be separated in a reasonable manner, the economics of the process would appear even more attractive. The economics would appear more attractive since the proposed price for the dipentene was ten cents per gallon as fuel and the industrial price for dipentene is fifty cents per gallon when the purity is from 50 to 80 per cent dipentene.

APPENDIX

Table VII; Limiting Binary Composition in Still Pot for

Removal of 95% Pure Product

Desired Product	Theoretical Plates	Reflux Ratio	Binary	Mass Fraction More Volatile	
				Unadjusted	Adjusted
Alpha-pinene	24	2.5:1	Alpha-pinene	0.750	0.735
		10:1		0.613	0.576
		20:1	Beta-pinene	0.546	0.495
	36	2.5:1		0.756	0.745
		5:1		0.620	0.596
		10:1		0.559	0.529
		20:1		0.483	0.440
	45	5:1		0.636	0.609
		10:1		0.570	0.529
		20:1		0.493	0.443
Delta-3-carene	36	5:1	Delta-3-carene	0.820	0.810
		10:1		0.690	0.670
		20:1	Dipentene	0.680	0.650
	45	2.5:1		0.810	0.800
		5:1		0.785	0.765
		10:1		0.703	0.678
		20:1		0.663	0.609