

THE DESIGN OF A PLANT TO PRODUCE TERPINEOL  
FROM DESTRUCTIVELY DISTILLED PINE WOOD WASTES

by

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## I. INTRODUCTION

The industry involving derivation of turpentine and associated chemicals from pine wood began in the United States in Maine at the beginning of the seventeenth century. That industry has spread greatly and with its center now located in the southeastern section of the country. Of the many variations of the methods for obtaining turpentine from pine wood, four general processes may be given to represent the field. These include steam distillation of the oleoresin exuding from living trees, steam distillation of pine wood wastes, destructive distillation of pine wood wastes, and solvent extraction of the waste product, pine chips, of the sulfate paper process.

The pine industry had its beginning centuries ago due to the demand for turpentine and rosin or pitch. Approximately a half century ago commercial interest was accorded the derivatives from pine products obtained by some type of chemical processing. The present-day problems of the pine industry are those of any new industry, that is, the furtherance of research of large scale demand to warrant commercial production of chemicals, development of processes, and design of equipment to carry out the processes and operations.

Of the several chemical derivatives of pine wood now produced to supply commercial demand,  $\alpha$ -terpineol is of importance because of its many uses in the perfume and soap industries. Due to the large number of processes for production of  $\alpha$ -terpineol from pine wood, the problem is presented as to which is the most practical. The solution will depend on development of processes and plant location, design, and operation.

The specific purpose of this investigation is to develop a method of production and design a plant to produce 100 pounds of  $\alpha$ -terpineol per day as a main product with closely-associated terpenes as side products.

## II. LITERATURE REVIEW

### History and Economics

In 1553 Hakluyt was the first to advise England to colonize in the Western World when he wrote of America as a land of: "... an abundance of pine and firr trees to make deale boards and mastes, pitch, tar, and rosen ...." (42). Thirty-five years later when England became ruler of the seas, naval stores were in great demand for ship repairs. Thus, it was only one year after Jamestown was colonized in 1607 that naval stores were exported from America (61), although Jamestown was originally a business venture to "dig gold, loade gold, and ship gold". Due to continued and greater exports of pitch, tar, and rosin, England was able to hold its naval supremacy. To insure this constant supply of much-needed naval stores England had to pass navigation laws in America in 1704, as the Americans were shipping to other buyers at higher prices (42).

The naval stores industry in America began moving south and in 1734 North Carolina was reported as being the greatest producer of naval stores in the country, and at that time America was exporting about 200,000 barrels of pitch, tar, and rosin per year (38)(61). Interest was boosted in the industry when the copper still was first used in 1834

to simplify distillation. During the War of Secession, Florida, Georgia, and South Carolina began producing turpentine and rosin. By 1900, Alabama, Mississippi, Louisiana, and Texas started production of naval stores with Georgia leading (61)(75). In 1900 H. T. Yaryan of Toledo, Ohio, began a series of experiments which led to the erection of a plant in Gulfport, Mississippi, to obtain turpentine and rosin from logging wastes (75)(82). By 1913, Florida was the leading producer of naval stores in the United States, with the main process being that of steam and solvent recovery (70)(75)(96). At the same time destructive distillation began to show importance and became the third process for the removal of naval stores from the pine tree.

In the graph, Turpentine Cost vs. Years, on page 5, turpentine cost has been plotted against time to indicate the effect of the national economy on the naval stores industry (5). Turpentine has been chosen as a representative product of the industry.

### Processes

Steam Distillation of Oleoresin. The first process for removal of turpentine and rosin from the pine tree is believed to have been introduced thousands of years ago in the forests of Syria to produce naval stores for the seafaring

*Turpentine Cost vs. Years*

*for  
1916 - 1945*

*9 Jan. 1947*

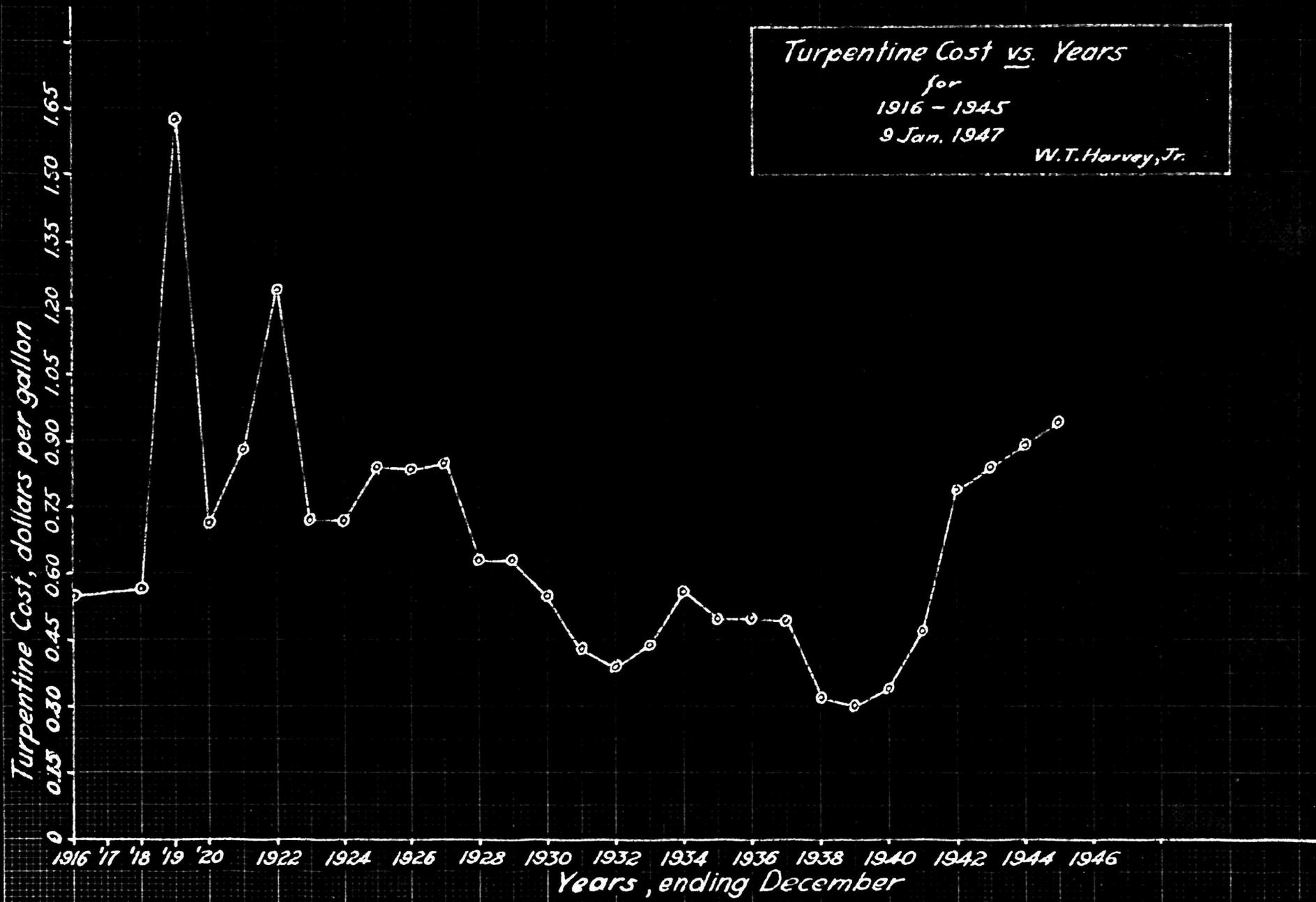
*W.T. Harvey, Jr.*

*Turpentine Cost, dollars per gallon*

*0 0.15 0.30 0.45 0.60 0.75 0.90 1.05 1.20 1.35 1.50 1.65*

*1916 '17 '18 '19 '20 1922 1924 1926 1928 1930 1932 1934 1936 1938 1940 1942 1944 1946*

*Years, ending December*



Phoenicians. The method of production has remained essentially the same with the addition of many features to facilitate improvement of yields. The process consists of making incisions in the bark of the living tree and collecting the gum which flows from the incision, this time of flow being between the months of March and September <sup>(75)</sup>. The collected sap is distilled in a copper still with water and turpentine passing over as distillate and rosin remaining behind as residue in the stillpot. The rosin may be removed or it may be steam distilled to increase the yield of turpentine <sup>(22)(61)(70)(75)(84)</sup>. The average composition of the collected sap or gum is 68 per cent rosin, 20 per cent turpentine, and the remaining 12 per cent is water <sup>(97)</sup>. In the crop year April 1940-March 1941, the amount of turpentine produced in the United States by distillation of the oleoresin exceeded 60 per cent of the total production.

Steam Distillation of Pine Wood Wastes. The continued yearly tapping of pine tree eventually kills the tree and those industries concerned with processing the oleoresin move to virgin or replanted forests. Due to the constant exposure the dead tree decays and the inner gum ducts which still contain some sap are exposed. During the weathering process some of the gum present in the oleoresin is broken down into monocyclic and dicyclic compounds, the mixture of

which is called pine oil and is found only in dead pine or  
(60)(71)(83)(98)  
pine wood wastes .

The process for removal of chemicals from pine wood wastes by the steam distillation method (more commonly called the steam and solvent recovery method) is as follows: The pine wood wastes selected are first sent through hoppers and shredders which reduce the wood in size and facilitate extraction of entailed pine chemicals. The resulting chips are loaded into a battery of extractors where they rest on a false bottom, through which live steam is introduced for a certain period of time. At the end of that operation, the steam is shut off and the chips are treated with a selected solvent such as naphtha or a volatile cut of gasoline. The use of a solvent is a recent improvement which insures more complete extraction of chemicals present. The product of the extraction battery is sent through several concentrating evaporators and then to a fractionating column where the solvent is recovered and recycled to the extraction set. In the evaporator immediately preceding the fractionator, rosin is drawn off as the residue. The mixture leaving the fractionating column as residue is sent into a steam still and fractionated into three components: turpentine, pine oil, and an intermediate fraction of terpenes. This latter fraction consists mainly of dipentene, accompanied by p-menthane,

p-cymene, terpinene, and others of that boiling range (175-205°C.) (22)(58)(59)(75)(82)(84)(96). The expended chips are sent to the boilers to be used as fuel in the production of steam for extraction. The flow diagram for the process is given below.

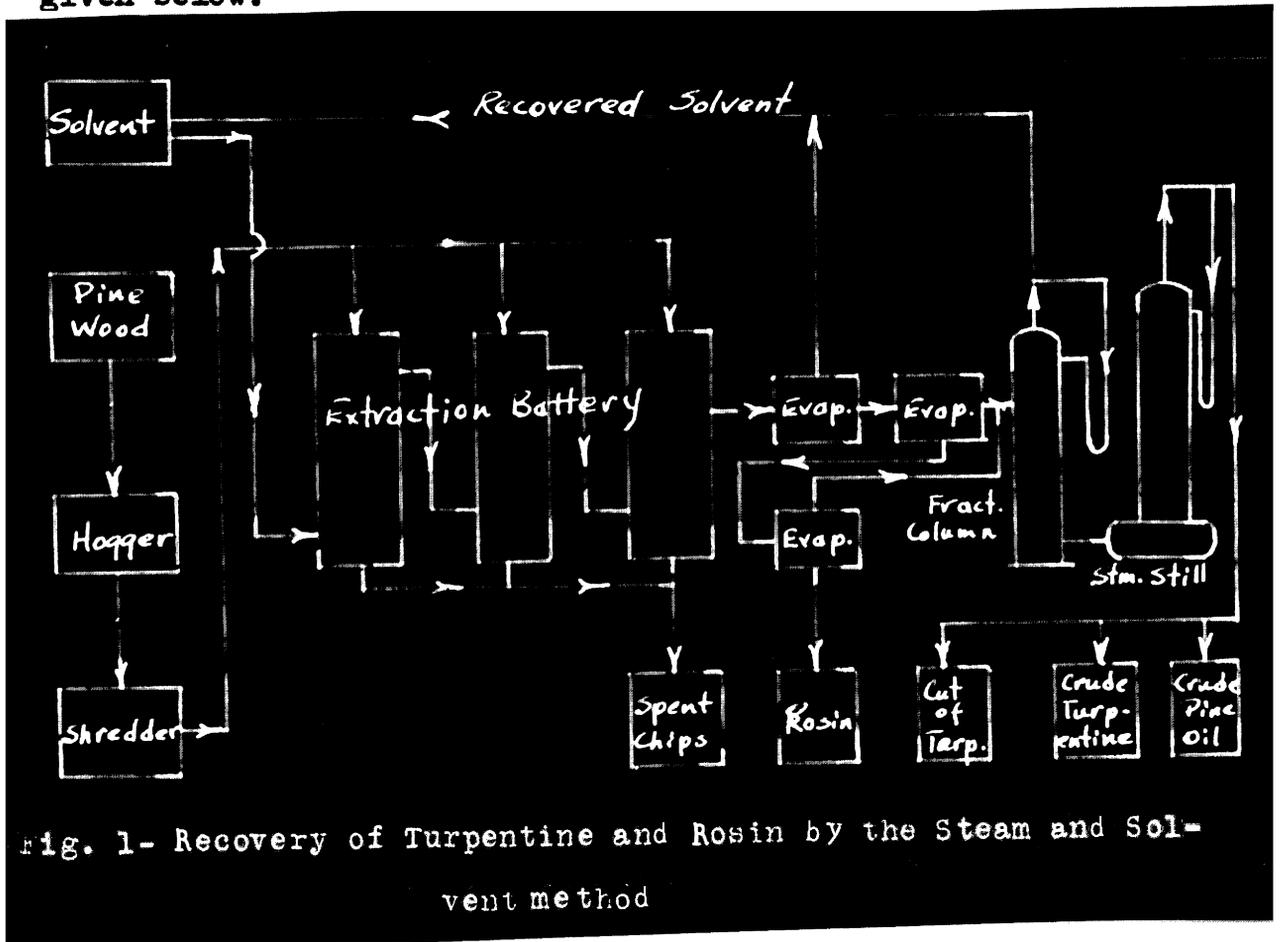


Fig. 1- Recovery of Turpentine and Rosin by the Steam and Solvent method

Distillation of Sulfate and Sulfite Paper Wastes. In the reactor of the sulfate, or Kraft, paper process where pine chips are treated, the introduction of live steam liberates low boiling vapors containing turpentine and pine oil; and, upon condensation of these vapors, an oily top

layer formed is removed and fractionated to obtain the pine chemicals present. The yield of non-aqueous substances is about 2 to 10 gallons per ton of paper pulp produced. The oily layer consists of 50 to 60 per cent turpentine, 10 to 20 per cent pine oil, and the remainder of sulfur compounds. The turpentine and pine oil derived by fractionation of the oily layer will contain sulfur in the form of mercaptans (22) which is removed using a hypochlorite or ethylene diamine (61)(84)(85)

In the sulfite paper process a similar method of producing pine chemicals from waste vapors is employed (84). The vapors from the digester or reactor are condensed and distilled. The product is p-cymene, rather than turpentine, and it has a number of uses as a solvent, as an intermediate in organic synthesis, and as an ingredient in metal polishes (28). The difference in the two products results from the use of spruce in the sulfite paper process and the use of pine wood in the sulfate process. The yield of p-cymene is between 0.36 and 1.0 gallons per ton of paper pulp produced (49).

Destructive Distillation of Pine Wood Wastes. In the selection of pine wood wastes to be used in the extraction of chemicals it is naturally advantageous to choose wood (82) having a high gum content. Sherwood classifies the pine

tree and its gum content by the part of the tree from which it comes: viz.- (a) the stumps are very rich with the exception of the tap root, (b) the trunk of the tree up to the first limbs and the limbs themselves contain only small amounts of the pine chemicals, and (c) knots and other irregularities in the grain of the wood are very rich in the desired gum.

Pine wood to be removed from the ground is either pulled out by tractor and special equipment <sup>(60)</sup> or it is dynamited <sup>(22)</sup>. A combination of the two methods is now generally employed so that all the pine wood is removed from the ground, leaving it suitable for agriculture; and dynamiting the removed wood will remove all bark and outer rotten wood and reduce the size of the inner, gum-bearing wood.

The pine wood is shipped to the plant and there it is further reduced in size by hoppers and shredders to about five inches in length and one-half inch in diameter <sup>(70)</sup>.

The wood is charged into retorts arranged in long rows. The retorts may be internally or externally heated, horizontal or vertical in position, drained or not drained <sup>(22)</sup>.

<sup>(51)</sup> Nealey describes externally gas-heated, horizontal, non-drained retorts which operate on a 16 hour heating period, and that period is followed by eight hours of cooling. The water which is first given off in the retort as steam

prevents the chemical vapors which follow from coming into contact with the hot walls of the retort and thus decomposing<sup>(3)</sup>. These chemical vapors leave the retort and are condensed, the liquid being collected in wooden tubs. Non-condensable vapors are sent back to the retort to be used as fuel in the heating or to the steam plant<sup>(8)</sup>. The first period of condensation yields light oils; later pyroligneous liquors condense and settle to the bottom of the container. Finally, heavier oils are condensed and displace the pyroligneous liquor which rises to a position between the layers of light and heavy crude oils. The heavy and light crudes are separated by decantation, combined, and subjected to steam distillation. The distillate contains crude turpentine, dipentene, and pine oil. These fractions are combined and the mixture is bleached with sulfuric acid and again fractionated to yield wood naphtha, turpentine, dipentene, pine oil, and creosote, in order of distilling temperature range. The creosote must be neutralized before it can be sold for commercial use<sup>(22)(51)(59)(61)(75)(83)(84)</sup>

A qualitative flow sheet for the destructive distillation of pine wood wastes follows (51)(83)(96)

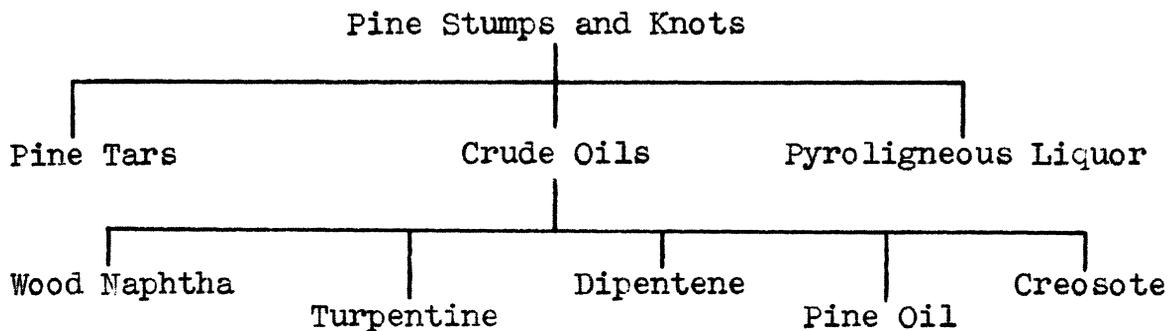


Fig. 2- Production of Pine Products from Destructively Distilled Pine Wood Wastes

### Product Economics

Terpene Chemicals. The chemicals derived from pine wood belong to the general family called terpenes and their production begins with pine oil, turpentine, and dipentene, the source of which is given in Fig. 2- Production of Pine Products from Destructively Distilled Pine Wood Wastes. Though there are several methods of arriving at the final product, in this case terpeneol, the qualitative flow remains essentially the same.

Relation of raw materials to each other with terpineol as an end product is as follows:

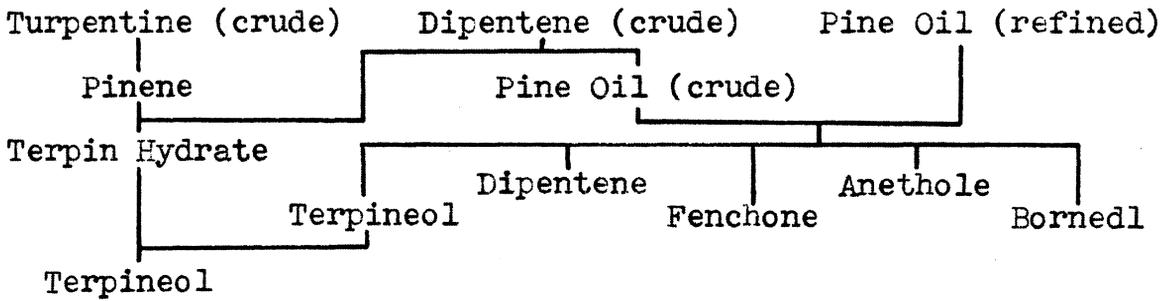


Fig. 3- Relation of Destructive Distillation Raw Products with Terpineol as the Final Product

(99)

Factors Affecting Investigation or Research. Tyler

suggests investigation or research to be coordinated with the following possibilities in mind:

- 1) New uses for present products
- 2) New products from present materials and techniques
- 3) Demands for specific product or service
- 4) Latent or generally unrecognized needs
- 5) Suggestions, ideas, and inventions arising outside

the organization

6) Savings through improvements of present products and processes

- 7) Development of radically new techniques
- 8) Development of new raw materials
- 9) Fundamental research

With all the above factors remaining equal the investigation will have to be made on the basis of development of side products in addition to the development of the main product, which is terpineol.

Physical Aspects

In the order of their appearance in the flow sheet for preparation of terpineol from pine wood wastes by destructive distillation the physical procedure includes hogging and shredding, destructive distillation, decantation, and fractional distillation.

Hogging and Shredding. The size of wood with which the retort is to be charged is dependent upon several conditions. If one of the main products is to be charcoal, the wood will be cut to size about two inches in diameter and four to five feet long <sup>(60)</sup>. The pine wood may be reduced with hoppers and shredders to small sizes if desired <sup>(64)</sup>, ranging from one-half to one-fourth inches in diameter and about one inch long. This size is used in the steam and solvent recovery method <sup>(59)</sup>. The smaller size of wood insures access to the small gum ducts present in the wood <sup>(43)</sup>, and thereby decreases the time required for complete destructive distillation.

Destructive Distillation. Destructive distillation is defined <sup>(63)</sup> as the operation in which the material under process first undergoes thermal decomposition and the products are then withdrawn as vapors for recovery.

In the pine industry destructive distillation is performed in horizontal steel drums or retorts. These retorts may be fired internally or externally, the latter method having proved to be the more economical in terms of cost per unit of recovered product <sup>(22)</sup>. In the process a tar will be formed in the bottom of the retort and this residue may be drained off or will, upon continued heating, yield a hard cake-like mass in the retort which must be scraped out

periodically.

(98)  
Toch asserts that temperature control is the greatest singly factor in destructive distillation. The important rule is that it is essential to remove turpentine and pine oil before the temperature at which the resins and the wood fibers begin to decompose is reached. That temperature of decomposition at standard conditions is approximately 450° F. According to Bain (8) there is always some chemical change in pinene during destructive distillation of pine wood wastes. The major change is the isomerization of the pinene present to form dipentene and the amount of isomerization will depend on design and operation of equipment.

Decantation. The condensed vapors from destructive distillation will, upon standing, separate into three definite layers due to their differences in density and their immiscibility, with pyroligneous liquor being held between layers of light and heavy distillate fractions. Separation of the three layers consists simply of skimming off the top and draining off the bottom fractions from the settling tank, leaving the pyroligneous liquor behind and giving (51) crudes of very pure state .

Fractional Distillation. Fractional distillation, or rectification, is defined (63) as a distillation carried out in such a way that the vapor rising from a still comes in

contact with a condensed portion of vapor previously evolved from the same still. A transfer of material and an interchange of heat result from this contact, thereby securing a greater enrichment of the vapor in the more volatile components than could be secured with a simple distillation operation using the same amount of heat.

Generally, fractional distillation may be divided into two parts: binary and complex or multicomponent mixture distillation. The two divisions vary in that the latter consists of one volatile constituent with two or more less volatile constituents. The following theory of the fractionation column is based entirely upon binary mixtures (77) (7)(63)

Boiling Point Diagrams. Figure 4, Boiling Point Diagram, represents the boiling point and equilibrium relationships, at constant pressure, of all mixtures of liquid A (boiling point  $t_A$ ) and liquid B (boiling point  $t_B$ ). Liquid A is the more volatile liquid. Any point on the upper curve is the composition of that vapor (e) at that temperature ( $t_1$ ). The composition of that liquid in equilibrium with the vapor at temperature ( $t_1$ ) has the composition (d). Any two points on the horizontal line, such as (x) and (y), represent the composition of liquid and vapor, respectively, in equilibrium at the temperature of the line passing

through them. This phenomena has been proven experimentally, and is probably due to perfect agitation incident to boiling (107)

. For all points above the vapor line, such as (a), the mixture is entirely vapor. For all points below the liquid line, such as (b), the mixture is entirely liquid. Between the two lines any point, such as (c), is a mixture partly liquid and partly vapor.

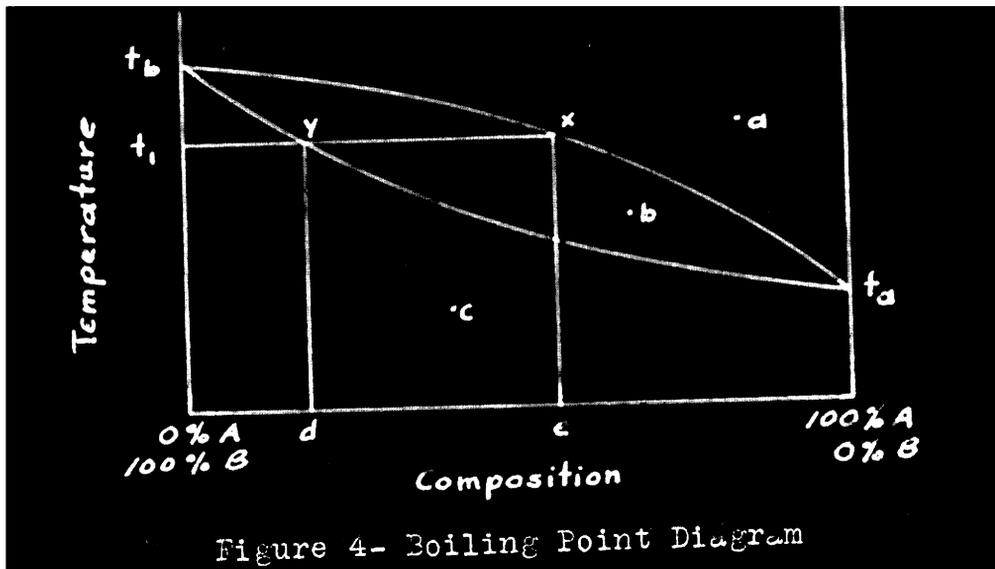
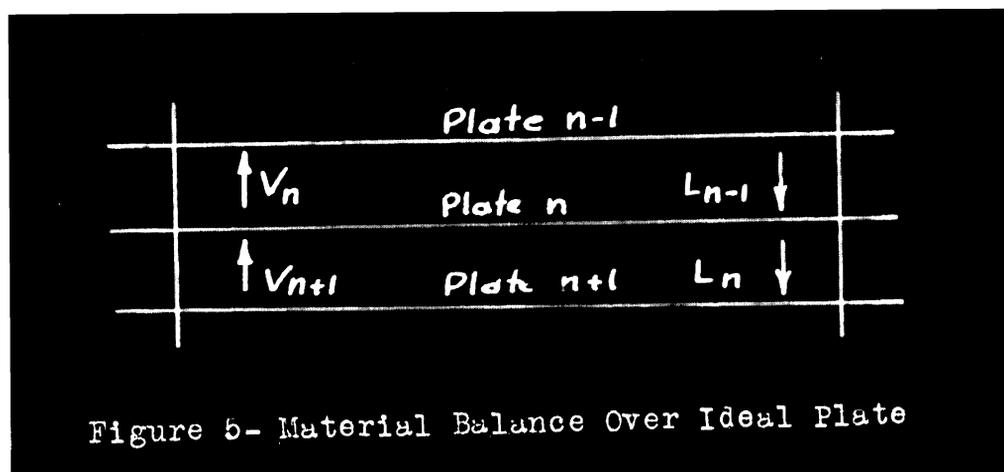


Figure 4- Boiling Point Diagram

Referring to Figure 4, Boiling Point Diagram, if a liquid mixture of composition (d) is heated it will begin to boil at temperature ( $t_1$ ), and the composition of the resulting vapor is represented by point (e). As soon as an appreciable amount of the mixture has vaporized the composition is no longer that of (d) and the point (x) tends to move toward  $t_b$ .

Theory of the Fractionating Column. The performance of an actual column may best be understood by comparing it with an ideal column. An ideal column is made up of theoretical plates and each plate fulfills the requirement that the vapor rising from the plate is in equilibrium with the liquid falling from the plate to the next lower plate.

Each theoretical plate has four streams of material entering or leaving it. A stream of vapor from below and a stream of liquid from above are entering the plate, and a stream of vapor to the next higher plate and one of liquid from the plate to the next lower plate are leaving this theoretical plate. This operation is shown in Figure 5, Material Balance Over Ideal Plate.



As has already been explained concerning Figure 4, Boiling Point Diagram, the stream  $V_n$  is richer in the more

volatile component and  $L_n$  is richer in the less volatile component. It follows then that plate  $n-1$  will be richer in the more volatile component with plate  $n-1$  being richer in the less volatile component.

A material balance may be written across plate  $n$  as follows:

$$V_{n+1} + L_{n-1} = V_n + L_n$$

Since, by definition of a theoretical plate,  $V_n$  is in equilibrium with  $L_n$ ,  $V_{n+1}$  is not in equilibrium with  $L_{n-1}$  and their tendency to approach that state upon close contact results in the loss of component A (the more volatile) from  $L_{n-1}$  to  $V_n$  and the heat necessary to vaporize A comes from condensation of component B (the less volatile) causing  $L_n$  to obtain more component B from  $V_{n+1}$ . The heat balance for the ideal plate is then, basically, the latent heat in vapor  $V_{n+1}$  equaling the latent heat in vapor  $V_n$ .

Reflux. The condensed vapors returned to the column to accomplish rectification are called the reflux. Usually reflux is referred to numerically and that number represents a ratio of the amount of liquid passing down through the column to the amount of the liquid being drawn off as product. An increase in reflux ratio increases the number of plates required to obtain a desired product and will decrease the amount of product obtained per unit time.

Plate Efficiency. There are two types of plate efficiency. The first is an average for the entire column and may be found by dividing the number of theoretical plates required to produce a desired product by the number of actual plates that deliver that product. The other type of plate efficiency is based on the individual plate and is calculated by the following equation:

$$E = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} 100$$

where

$y_{n-1}$  = composition of the vapor rising to the plate

$y_n$  = composition of the vapor leaving the plate

$y_n^*$  = composition of the vapor in equilibrium with the liquid leaving the plate

Factors affecting the plate efficiency include effectiveness of contact between vapor and liquid, plate design, and vapor velocity through the column.

Determination of Compounds. For accurate determination of compounds several methods are used not only to identify the compound but also to ascertain its degree of purity or concentration. The more widely used methods of identification are refractive index, boiling point, specific gravity and melting point.

Refractive Index. Refractive index is the ratio of the sine of the angle of incidence to the sine of the angle of refraction which occurs when a beam of light passes through a liquid and is bent due to the change in density of air to the liquid. That ratio is measured by means of an Abbe refractometer which also indicates the temperature of the sample when its index is recorded (93).

(2)  
Boiling Point. The determination of boiling point consists of heating the unknown liquid to its boiling point, the point at which the vapor pressure of the liquid equals that of the atmosphere, and recording the temperature of the vapor. All pure compounds have a definite boiling point at a specific pressure. A correction for the thermometer must be made as all the mercury in the stem is not at the same temperature. *The portion of the mercury above the cork is cooled by the surrounding atmosphere, and the registered temperature is below that of the vapor in the column.* This error can be corrected by adding a "stem correction" calculated by the formula:

$$\text{Stem Correction (in degrees)} = 0.000154(t - t')N$$

where

N = number of degrees on the stem of the thermometer from the lower exposed level to the atmosphere read.

t = temperature read.

t' = average temperature of the exposed mercury column.

Specific Gravity. Specific gravity is most commonly determined in the laboratory using a pycnometer, which is a bottle having a specific volume. The tare weight of the unknown is obtained by difference and compared with the weight of water at the same temperature (91).

Melting Point. Melting point is determined by inserting fine crystals of the unknown solid in a capillary tube and fastening the tube to the bulb of the thermometer. The thermometer is inserted in a constantly-stirred, transparent, non-inflammable liquid and heated slowly. The point at which the solid melts is reached when the opaque solid becomes clear (92). To obtain accuracy, a thermometer stem correction must be made.

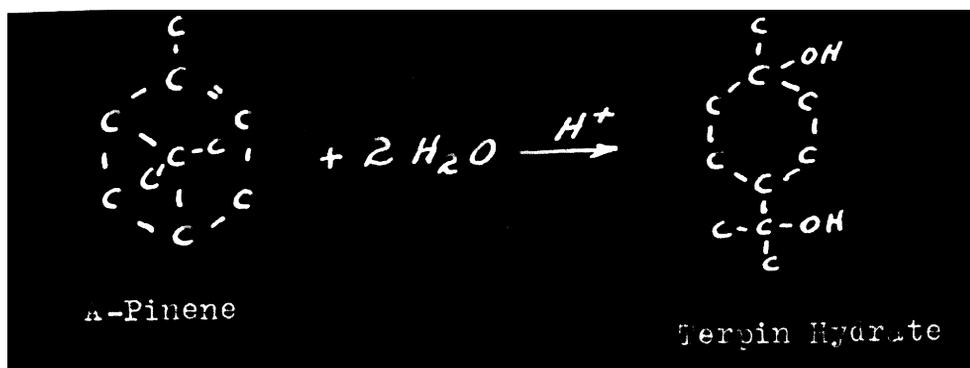
### Chemical Aspects

In the entire flow sheet for derivation of  $\alpha$ -terpineol from pine wood wastes as presented on page 13, Figure 3, Relation of Destructive Distillation Raw Products with  $\alpha$ -Terpineol as the Final Product, the only chemical reactions involved are in obtaining terpineol from pinene and from dipentene.

A-Pinene to Terpin Hydrate. The production of terpin hydrate from  $\alpha$ -pinene proceeds to according to the equation given on page 24.

(1)

Acharya and Wheeler give the following procedure for producing terpin hydrate from  $\alpha$ -pinene: "Pinene (1 part) and sulfuric acid (22-25%; 1.75 parts) are shaken vigorously for 35-40 hours with gelatin (2-2.5%), which acts as an emulsifying agent, when sandy crystals of terpin hydrate are copiously formed. At the outset a few crystals of terpin hydrate are added to act as nuclei for crystallization. The liquid is filtered to remove the terpin hydrate (0.44-0.45 parts) and the filtrate is again shaken for 5-6 hours with dilute sulfuric acid (22-25%; 0.25 parts). The solid is collected and washed with water and treated with dilute sodium carbonate solution, filtered, dried, and weighed. Yield of terpin hydrate, 40.3% of theoretical; m.p. 116-117° C.; m.p. of pure compound 117°."

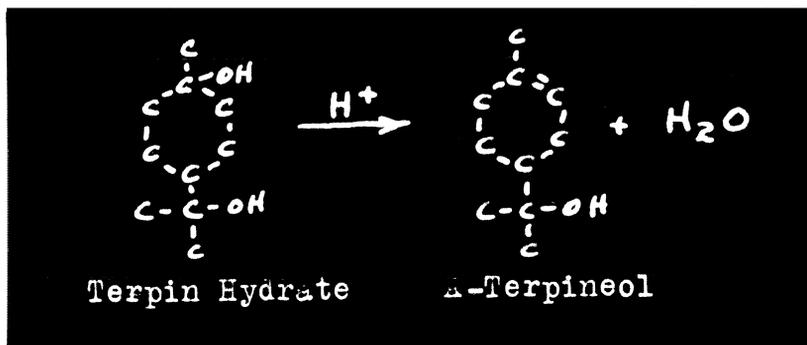


(21)

Fornet uses dilute sulfuric acid in producing terpin hydrate from  $\alpha$ -pinene and he also states that some  $\alpha$ -terpineol will be formed in the reaction. Gregory (34) states that terpin hydrate is formed from turpentine upon contact

with nitric acid and alcohol. This is, essentially, formation from  $\alpha$ -pinene since the latter occurs in turpentine from 80-92% (10)(43)(46)(62). Kaminski (45) adds that a more pure terpin hydrate may be obtained by washing Acharya and Wheeler's solution with turpentine before crystallization. (87) Simonsen advocates using sulfuric acid (25 per cent) on an alcoholic solution of turpentine (pinene) to produce terpin hydrate.

Terpin Hydrate to  $\alpha$ -Terpineol. The production of  $\alpha$ -terpineol from terpin hydrate proceeds according to the following reaction:



(1)

Acharya and Wheeler found the following optimum conditions in producing  $\alpha$ -terpineol from terpin hydrate: Terpin hydrate is boiled under reflux for 6-7 hours with twice its weight of 0.5% oxalic acid solution. The yellow upper oily layer containing terpineol is separated, the fraction boiling at 200-214° C. being collected. Yield 89.4% of theoretical." Gregory (34) used phosphoric acid in the

dehydration of terpin hydrate to form terpineol, as does  
(21)

Fornet . Fornet also states that some  $\beta$ -,  $\gamma$ -, and l-ter-  
pineol are formed in addition to the primary terpene.

(76)  
Robert advances use of phosphoric or sulfuric acid as a  
source of the hydrogen ion in the above equation. Germuth (23)

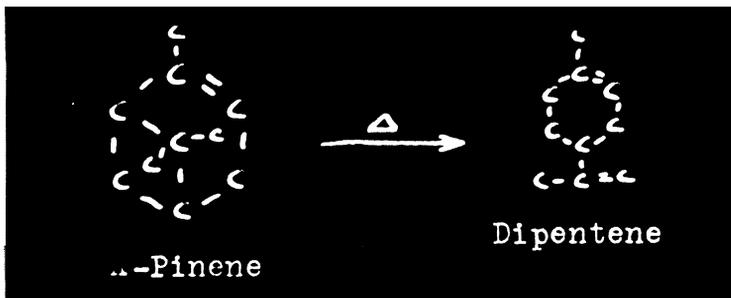
produced  $\alpha$ -terpineol directly from  $\alpha$ -pinene in glacial ace-  
tic acid in the presence of benzenesulfonic acid containing  
1.5 mols of water. Refluxing at 95° C. for one hour resul-  
ted in a conversion of 73% of the theoretical. Hercules  
(39)

Powder Company patented a process wherein  $\alpha$ -pinene was  
treated with an acid mixture of formic (60-75%) and phos-  
phoric (20-40%) acids to produce  $\alpha$ -terpineol. Flovitzky (20)

prepared  $\alpha$ -terpineol from  $\alpha$ -pinene by the action of sulfur-  
ic acid in acetic acid or alcoholic solution. According to  
(13)

Brooks and Humphrey these latter reactions are limited  
since polymerization takes place with the formation of high  
molecular hydrocarbons if a large proportion of H<sub>2</sub>SO<sub>4</sub> is  
used.

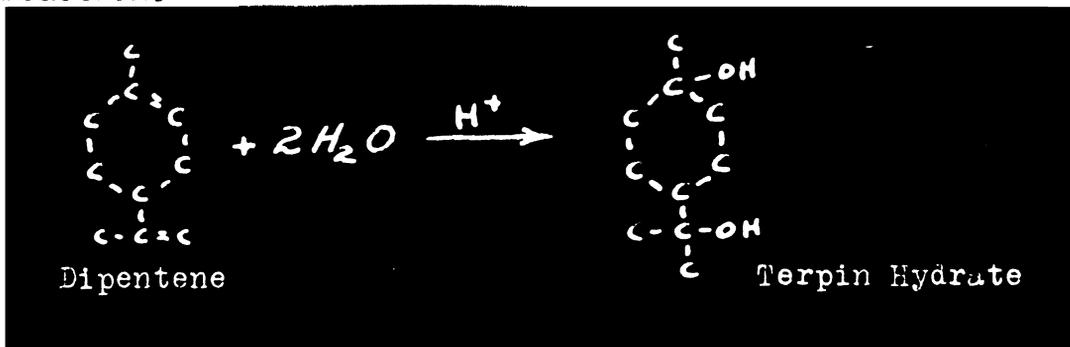
$\alpha$ -Pinene to Dipentene. The production of dipentene from  $\alpha$ -pinene proceeds according to the following reaction:



(12)

Berthelot found that when  $\alpha$ -pinene was heated under pressure at 250-270° C. dipentene was formed. This investigation was substantiated by Conant and Carlson (17) in their research concerning the apparent racemization of  $\alpha$ -pinene due to heating.

Dipentene to Terpin Hydrate. The production of terpin hydrate from dipentene proceeds according to the following reaction:



(9)

Baker states that the formation of terpin hydrate from dipentene is a two-step process. First, dipentene is treated with hydrogen bromide, and then with potassium hydroxide, the intermediate compound being a dihydrobromide.

(15)  
Cheronis states that the commercial process for producing terpin hydrate from dipentene consists of refluxing dipentene in a dilute sulfuric acid solution. According to (6)  
Aschen terpin hydrate is obtained in excellent yield by treatment of dipentene with sulfuric acid (50 per cent) at -6° C.

### Intermediate and Side Products

In the process of deriving terpineol from pine wood wastes by destructive distillation, many steps in procedure and several side products are encountered. As practicability in design demands, these steps, or intermediates, and side products will vary; but the flow diagram of the process will generally be a composite of the flow diagrams on pages 12 and 13, Figures 2 and 3, Production of Pine Products from Destructively Distilled Pine Wood Wastes and Relation of Destructively Distillation Raw Products with A-Terpineol as the Final Product, respectively. The physical and chemical constants for those intermediate and side products are listed in Table 1 on page 32. A presentation follows on the uses, source, etc., of the less common of these products.

Anethole. Anethole, or anise camphor, is a high-boiling fraction of pine oil (58)(60)(83) and has an odor of licorice. It is used in flavoring compounds, the perfume industry, and in color photography. The compound is not sold in the pure form but in two grades: technical and N. F. (4)  
(25)

Borneol. Borneol, or borneo camphor, is a high-boiling fraction of pine oil (58)(60)(71)(83) and has a camphor-like odor. It is used in the manufacture of synthetic camphor, in the perfume industry, and in medicine (26)

Charcoal. In many plants destructively distilled pine wood yields charcoal as the main product, with escaping gases being caught as the side products (22)(51). The uses of charcoal include catalysis, decolorization, explosives, fuel, and many others (27).

Creosote. Creosote is a high-boiling fraction of light crudes, the latter being a weight fraction of destructive distillation (22)(51)(96). Creosote has a smoky odor and its principal use is in ore flotation where it is used as a frothing agent (51).

Fenchone and Fencyl Alcohol. Fencyl alcohol is listed (11)(29) as being a pine derivative while fenchone is listed as a ketone found in oil of fennel and oil of thuja. (50)  
McClure states that by a special process fencyl alcohol

is automatically converted to fenchone. Speh<sup>(96)</sup> mentions this process, but he does not go into detail. Both of these compounds are used as chemical solvents<sup>(29)</sup>.

Laksol. Laksol is a brand name for the low-boiling fraction of light crudes<sup>(32)</sup>. The main uses of Laksol are as a lacquer diluent and a solvent<sup>(51)</sup>.

Pine Oil. Pine oil is a fraction of light crudes removed between the temperatures of 188° and 235° C.<sup>(4)(30)(71)</sup>  
(83)(97)(98)

. Pine oil may be compared to crude petroleum in that both are physical mixtures of many compounds, each of which has a definite and distinguishing boiling point.<sup>(60)</sup> Palmer lists the more important compounds in pine oil in order of boiling point as follows:  $\alpha$ -pinene, camphene, p-menthane, limonene, dipentene, cineol,  $\alpha$ -terpinene, terpinolene, fenchol, borneol, "menthanols",  $\alpha$ - and  $\beta$ -terpineol, terpinenols, the phenol ethers, methyl chavicol, and anethole. Pine oil has a characteristic pine odor and is used as a source of terpenes, flotation agent (wetting), germicide, and liquid soaps<sup>(4)(30)(71)</sup>.

Pine Tar. Pine tar is a mixture of phenols and is a weight fraction of destructive distillation<sup>(33)(51)(96)</sup>.

It has a strong tarry odor and taste and is used in medicine, in skin treatment, and when not refined, it is used in roofing compounds.

Pyroligneous Liquor. Pyroligneous liquor is a weight fraction of destructive distillation of either hardwood or softwood <sup>(31)</sup>. It has a strong furfural odor and contains acetic acid. The main use of pyroligneous liquor is in the manufacture of methyl alcohol; but in destructive distillation of softwood, it is sometimes used to neutralize the light crudes after they have been bleached with caustic.

PHYSICAL PROPERTIES OF SOME TERPENES AND RELATED WOOD CHEMICALS

NAME	Anethol	Borneol	Charcoal	Cressote	Dipentene	Fenchone	Fencyl Alcohol	Laksol	A-Pinene	Pine Oil	Pine Tar	Pyrosijne- ous Acid	A-Terpin- eol	Terpin Hydrate	Turpen- tine
FORMULA			C	mixt.				mixt.		mixt.	mixt.	mixt.			mixt.
MOL. WT.	148.2	154.25	12.01		136.1	152.33	154.1		136.23			51.1 (c)	154.25	172.23	
CRYST. FORM & COLOR	leafy/leaf.	colorl. cryst.	black amorph.	black	liq.	liq.	colorl. cryst.	colorl. liq.	colorl. liq.	amber liq.		y. liq.	colorl. cryst.	colorl. rhomb.	colorl. liq.
SP. GR.	0.991 <sup>20°</sup>	1.011 <sup>20°</sup>	0.3-0.6	1.2-1.7	0.847 <sup>15.5°</sup>	0.948 <sup>18°</sup>	0.952 <sup>20°</sup>	0.852-8 <sup>20°</sup>	0.878 <sup>20°</sup>	0.9005 <sup>20°</sup>		1.018-1.03	0.935 <sup>20°</sup>		0.8517-0.8889
M.P.	22.5°	208-9°	>3500°			5-6°	30-4°		-55°				35°	117-20°	
B.P.	235.3°	212-3°	4200°	>225°	175-6	193-5°	198-204°	86-150°	154-6°	188-220°			218-9°		153-77°
SOLUBL.	H <sub>2</sub> O v.sl. Al. ∞ sl. Ether ∞	v.sl. v.sl. v.sl.	i. i. i.	i. sl.s. sl.s.	i. misc. misc.	i. v.s. v.s.		v.sl.s. ∞ abs. ∞	i. s. s.				i. v.s. v.s.	0.4 <sup>15°</sup> 10.0 <sup>15°</sup> 1.0 <sup>15°</sup>	i. s. s.
REF. IND.	1.5535 <sup>20°</sup>				1.4755 <sup>20°</sup>	1.4625 <sup>20°</sup>	1.4626 <sup>20°</sup>		1.4665 <sup>20°</sup>	1.4797 <sup>20°</sup>			1.4762 <sup>20°</sup>		1.4684-1.4818
VISC.									1.3 <sup>25°</sup> (Ubbelohde)	3.0 <sup>25°</sup> (Ubbelohde)			25.8 <sup>25°</sup> (Ubbelohde)		1.3 <sup>25°</sup> (Ubbelohde)
CORROSION					nil (Cu)				nil (Cu, Sn)	nil (Cu)					nil

### III. EXPERIMENTAL

#### Plan of Investigation

General Plan. In general, the plan of investigation is to derive data from the destructive distillation of pine wood wastes and subsequent operations in order to design a plant producing 100 pounds of  $\alpha$ -terpineol per day and related chemicals.

Specifically, the plan will follow these steps: procurement of raw materials, hogging and shredding, destructive distillation, separation, A.S.T.M. distillation, fractional distillation, chemical processing, and plant design and location.

Procurement of Raw Materials. The pine wood wastes to be chosen for destructive distillation will be stumps and knots, primarily, since these parts of the tree contain the greatest amounts of pine chemicals. To facsimilate actual conditions, some trunk and limb fragments will be selected. All pine wood will be deadwood and in the process of decay.

Hogging and Shredding. The selected pine wood wastes will be reduced in size by hogging and shredding. All this work will be done manually due to lack of equipment and the relatively small amount of wood to be processed. A fairly uniform product will be obtained, ranging in size from

one-fourth to one-half inches in diameter and five to six inches in length. A representative sample will be chosen to determine moisture content of the wood.

Destructive Distillation. The processed pine wood wastes will be charged into an externally heated, kerosene and compressed air-fired, horizontal, muffle furnace. The furnace will be fired and the temperature of the retort raised at a rate of about five degrees per minute to the maximum temperature of 1000° F., at which temperature complete carbonization of the wood will be assured.

The gases issuing from the retort will be collected and passed through a water-cooled condenser with the condensate being removed from the collector periodically. Non-condensable vapors will be burned in the atmosphere after they pass through the condensate collector.

Data to be recorded will include: atmospheric temperature; atmospheric pressure; weight and moisture content of wood; temperature of furnace, vapors, condensate, water in and out of the condenser; weight of cooling water; volume and density of non-condensable vapors; weight of resulting charcoal; and the volume and density of distillate fractions.

Separation. The total distillate from destructive distillation will be mixed and allowed to settle for two hours. At the end of that time, the separate fractions will be

separated by draining off each layer individually. The bottom layer, or heavy crudes, will be removed first; the middle layer, or pyroligneous liquor, will be removed next; and the top layer, or light crudes, will be drained last. Each layer will be processed to determine its volume and specific gravity.

A. S. T. M. Distillation. The top layer containing light crudes will be batch distilled to determine the amount of liquid distilled at any temperature and the amount of residue remaining at the end of the distillation. By close control of heating, the liquid will be distilled at a constant rate with the temperature being recorded at each ten per cent of the original charge collected as distillate. These ten per cent portions will be collected separately and the specific gravity recorded for each. The volume of the residue will be recorded as being the difference between the charge and amount distilled, and its specific gravity will be determined.

Fractional Distillation. Fractional distillation will be performed using light crudes so that Laksol or wood naphtha, pinene, dipentene, and pine oil are obtained.

Apparatus. Fractional distillation will be performed in an apparatus consisting of a flask mounted by a rectifying column and a reflux condenser. The flask will be heated

with a rheostat-controlled heating unit. The rectifying column will be inside two larger columns, the smaller of these two will be wound with nichrome wire for heating the column and the larger column will be insulated by wrapping it with one-eighth inch asbestos cord. The rectifying column will be topped by a reflux condenser which will permit the varying of the reflux by varying the rate and height of cooling water passing through the condenser. The vapor will then pass over into a water-cooled condenser and into collector bottles.

Light Crudes. The light crudes distillate from the A. S.T.M. distillation will be charged into the fractional distillation flask and distilled at a constant rate. Aids in obtaining that constant rate will be reflux control and column heating. Distillate will be collected in constants amounts with vapor temperature being recorded with each fraction.

Upon completion of distillation the specific gravity and refractive index will be determined for each fraction and for the residue in the flask. The volume of the residue will be recorded as being the difference between the charge and the amount distilled.

The fractions will then be mixed which correspond to the boiling ranges of wood naphtha, of turpentine, of

dipentene, and of pine oil. The specific gravity, volume, and refractive index of each of the four resulting fractions will be determined and recorded.

Turpentine. The fraction of light crudes corresponding to the boiling-point range of turpentine will be fractionally distilled under the same conditions as above with resulting distillate being divided into fractions of wood naphtha, turpentine, and dipentene. This new turpentine fraction will be fractionated to obtain a pinene fraction with the remaining liquid being added to the dipentene portion.

Dipentene. The dipentene fraction will be fractionated in a manner similar to that previously described, with the resulting distillate being divided into a dipentene boiling-point range and a pine oil range. The latter will be added to the pine oil fraction obtained from the distillation of the light crudes.

Pine Oil. The pine oil mixture from the light crudes distillation will be distilled using the same procedure as was used in previous fractionations. The individual fractions obtained will be investigated by determining specific gravity, and refractive index. These data will be used in attempting to identify the compounds in pine oil and their respective amounts present.

Chemical Processing. Chemical reactions will be examined using pinene and dipentene as reactants and terpin hydrate as an intermediate compound to produce terpineol.

Pinene to Terpineol. The pinene fraction from the turpentine fractionation will be converted into terpineol using quantities of reactants proportional to the amounts used in the following procedure: two grams of benzenesulfonic acid and an equivalent amount of pinene will be dissolved in five milliliters of glacial acetic acid, one and one-half mols of water will be added, and the mixture will be refluxed for one hour. The highest temperature of reflux tried, to date, is 95° C., which produced a 73% yield of the theoretical. Reflux temperatures will be tried at 5° C. intervals above 95° to determine at which reflux temperature the reaction will produce the best results.

Dipentene to Terpin Hydrate. The dipentene fraction from the dipentene fractionation will be converted into terpin hydrate by refluxing the dipentene in a dilute sulfuric acid solution. Conditions for the reaction will be determined by changing the concentration of the sulfuric acid solution and the reflux temperature.

Terpin Hydrate to Terpineol. The terpin hydrate obtained from the hydrolysis of dipentene will be converted into terpineol using the following procedure: the terpin

hydrate will be refluxed for six to seven hours with twice its weight of 0.5% oxalic acid solution. The yellow upper oily layer formed in the reaction will be separated and fractionated, the fraction boiling at 200-214° C. being collected.

Plant Design and Location. On the basis of the preceding experimental work and data obtained, a plant to produce 100 pounds of terpineol per day will be designed. Material and heat balances will be calculated for each operation. On the basis of these balances, equipment will be designed, selected, and located in the plant; the cost of buying, installing, and maintaining the equipment will be calculated; and the operating and depreciation costs will be computed.

Considering raw materials, market, transportation, labor, plant requirements, and power, the location of the plant will be selected.

### Materials

Acid, Acetic, glacial. "Baker's Analyzed", C. P., lot no. 82646, ap. gr. 1.049, m. p. 16.6° C., obtained from Phipps and Bird, Inc., Richmond, Virginia.

Acid, Benzene sulfonic. Pure, m. p. 44-50° C., contains one molecule of water of hydration, obtained from Fisher

Scientific Co., Pittsburgh, Pa.

Acid, Hydrochloric. "Baker's Analyzed", C. P., lot no. 32546C, sp. gr. 1.19, obtained from Phipps and Bird, Inc., Richmond, Virginia.

Acid, Sulfuric. "Baker's Analyzed", C. P., lot no. 13047, sp. gr. 1.84, obtained from General Chemical Co., Front Royal, Virginia.

Ethyl Alcohol. 95%, U. S. P., obtained from U. S. Industrial Chemical Corp., Baltimore, Md.

Kerosene. Obtained from Standard Oil Co. of New Jersey, Christiansburg, Virginia. Used for fuel in destructive distillation.

Pinene. Distilled from Hercules steam distilled wood turpentine, b. p. 153-155° C. at 715 mm. Hg., abs.; turpentine obtained from Blacksburg Hardware Co., Blacksburg, Virginia.

Pine Wood Wastes. Stumps, limbs, and knots; due to geographical location of source the wood was assumed <sup>(37)</sup> to belong to the genus Pinaceae, species pinus palustris (common pine); the wood was dead and in the process of decay; it was obtained from the east slope of Brush Mountain, five miles northwest of Blacksburg, Virginia.

Water, distilled. Distilled and obtained from the Chemical Stockroom, Chemistry Department, Davidson Hall, Virginia

Polytechnic Institute, Blacksburg, Virginia.

### Apparatus

A. S. T. M. Distillation Apparatus. The plan and specifications for the A. S. T. M. Distillation Apparatus may be found on page 74, Drawing No. 2.

Autoclave. The plan and specifications for the Autoclave may be found on page III, Drawing No. 4.

Balance, Analytical. Balance complete with chain, magnetic damper, notched beam, 200 gram per pan capacity, Virginia Polytechnic Institute identification no. 3x257 In 24, manufactured by Seederer-Kohlbrusch, Inc., Jersey City, N.J.

Balance, Solution. Two weighing beams, 20 kilograms total capacity, obtained from Central Scientific Co., Chicago, Ill.

Balance, Triple Beam. 610 grams total capacity, Virginia Polytechnic Institute identification no. 2x158 UOP 15B, manufactured by The Chemical Rubber Co., Cleveland, Ohio.

Bottles, Sample. Flint glass, threaded for aluminum screw cap tops, 8 ml. capacity, used for collecting samples from A. S. T. M. and fractional distillation runs.

Destructive Distillation Apparatus. The plan and specifications for the Destructive Distillation Apparatus may be

found on page 70, Drawing No. 1, Plan of a Destructive Distillation Furnace.

Fractional Distillation Apparatus. The plan and specifications for the Fractional Distillation Apparatus may be found on page 91, Drawing No. 3, Plan of a Laboratory Fractionation Column.

Pycnometers. 5 and 10 ml. capacity, unadjusted, fitted with ground in glass stoppers, obtained from Central Scientific Co., Chicago, Ill. Used for specific gravity determinations.

Refractometer, Abbe'.  $n_D$  range 1.3-1.7, Spencer refractometer no. 547, manufactured by Spencer Lens Co., Buffalo, N. Y.

Stirrer. Laboratory size, model #3, obtained from Eastern Engineering Co., New Haven, Conn.

Miscellaneous.

<u>Item</u>	<u>Size</u>	<u>No.</u>	<u>Material</u>	
Beakers	50 ml.	3	"Pyrex"	
	100 ml.	1	"	
	150 ml.	2	"	
Cylinders, graduated	25 ml.	1	"Exat"	
	250 ml.	1	"Pyrex"	
Flasks, Erlenmeyer	150 ml.	5	"	
Funnels, Separatory	250 ml.	1	"	
Pipettes, graduated	1 ml.	1	"	
	2 ml.	1	"	
	; plain	10 ml.	1	"Exat"
	; "	25 ml.	1	"
Test Tubes	40 ml.	6	"Pyrex"	
Thermometers	-20 to 110° C.	3		
	-10 to 360° C.	2		
Tubing	8 mm.	10 ft.	"Tygon"	
	10 mm.	8 ft.	Rubber	

Method of Procedure

Procurement of Raw Materials. The pine wood wastes to be used in destructive distillation were collected early in November, 1946. All wood collected was dead and in the process of decay; and all parts of different trees were select-stumps, limbs, and knots. The wood was stored in the Development Laboratory, Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia, to await reduction in size by hogging and shredding, prior to destructive

distillation.

Hogging and Shredding. The stored pine wood was reduced in size by hogging and shredding. These operations were performed manually due to the lack of equipment and the relatively small amounts of wood to be processed. The wood was sawed into five to six inch lengths and then split into splinters having a diameter of one-fourth to one-half inches. The product of size reduction was charged into the retort to be destructively distilled.

Destructive Distillation. A representative sample of the charged wood was chosen from the retort for moisture content determination. However, upon reaching the temperature of water vaporization it was found that not only water but also some organic chemicals present in the wood were removed. From subsequent operations (A. S. T. M. distillation) the water content of the wood was calculated to be 18 per cent.

The retort containing the reduced pine wood was closed and the cooling water to the vapor condenser was allowed to flow through that condenser. The compressed air valve to the burner was opened and kerosene was also admitted to the burner until the air-kerosene mixture issuing from the burner nozzle ignited. The burning mixture was adjusted to produce an approximate retort temperature rise of 5° F. per

minute. This retort temperature rise was held constant until the retort reached 450° F. The temperature was held at that point for about an hour. At the end of that time the temperature was again raised at the previous rate of 5° F. per minute by adjusting the air-kerosene mixture in the burner.

At the end of each ten minutes of operation the following data were recorded: retort temperature, vapor temperature, cooling water temperature in and out of the vapor condenser, condensate temperature, weight of cooling water through the vapor condenser, and volume of non-condensable vapor.

The temperature of the retort was raised to about 850° F., at which point the burner was shut off and the furnace was allowed to cool. During the time of cooling, the above data were recorded every five minutes until non-condensable vapor ceased to issue from the retort. The retort was not opened for 24 hours so as to prevent the cooling charcoal from coming into contact with air, and subsequently burning. The charcoal was then removed and its weight was recorded. The collected condensate was allowed to settle for 24 hours prior to separation of the two resultant layers.

During the process of destructive distillation, samples of the non-condensable vapor were taken, the time of collection being at the end of the first, second, and third hours of operation. Gas sampling bottles were filled with water and the vapor supply line was attached to one end of the bottle. Upon displacement of the water by the vapor, the bottle was closed and the vapor density was determined in the following manner: all the external surfaces of the collecting bottle were thoroughly dried manually and the bottle was weighed. The bottle was then flushed with water to remove all vapor, washed with alcohol, dried, and reweighed. After the latter weighing, the bottle was filled with distilled water which was drained and its volume measured and recorded. Atmospheric temperature and pressure was recorded at the time of each weighing.

The plan and specifications for the destructive distillation apparatus may be found on page 70, Drawing No. 1, Plan of a Destructive Distillation Furnace.

Decantation. The total condensate from the destructive distillation runs was allowed to settle for 24 hours. At the end of that time the condensate was observed to have separated into two layers, which were separated from each other using a separatory funnel. The top layer was black and the bottom layer was straw- or amber-colored. The two

layers were analyzed as to specific gravity using the following method: a clean, dry pycnometer, or specific gravity bottle, was weighed on an analytical balance. The bottle was then filled to the top with the unknown and the bottle's perforated glass stopper was inserted. The bottle was then reweighed and the temperature of the contained liquid was recorded.

A. S. T. M. Distillation. Each layer obtained from the decantation procedure was distilled in a batchwise method at a constant rate of five milliliters of condensate per minute. The amount of liquid charged was measured and upon distillation of each ten per cent (by volume) of that charge, the temperature of the vapor was recorded. Each ten per cent fraction was collected separately and the density of each was recorded using the pycnometer method. Distillation of both top and bottom layers produced a residue in the flask which appeared to be mainly creosote. The flask was heated and the creosote was poured into a weighed graduate. The amount of creosote and the weight of the graduate was recorded. Upon distillation of the top layer, it was observed that the condensate separated into two layers, the bottom being pyroligneous liquor and the top layer being light crudes. The original bottom layer from destructive distillation was pine tar oil, or heavy crudes.

The plan and specifications for the A. S. T. M. distillation apparatus may be found on page 74, Drawing No. 2.

Fractional Distillation. The light crudes fraction from A. S. T. M. distillation was charged into the laboratory size, fractionation column's heating flask. The reflux condenser was filled with cooling water and a constant head of running water was maintained at near capacity of the condenser by elevating the cooling water discharge tube. Cooling water was also allowed to flow through the product condenser.

The heating element under the distillation flask was turned on and controlled with a rheostat to give an initial low heat. The amount of heat was increased gradually until vapor began condensing in the reflux condenser. At this point the following data were recorded: time of initial condensation, and heating flask temperature. The vapors were allowed to form in the heating flask, rise in the rectifying column, and condense in the reflux condenser, thus obtaining total reflux, for five minutes. At the end of this time the cooling water head in the reflux condenser was decreased until vapors began passing up through the reflux condenser and into the product condenser. By adjusting the flask heater and the reflux condenser cooling water head, the condensate rate of flow was

held constant at seven milliliters per four minutes, a rate predetermined according to column design <sup>(52)</sup>. Upon collection of each seven milliliters of condensate, the following data were recorded: time of collection from start, flask temperature, and vapor temperature. As the vapor temperature rose, it became necessary to turn on the column heater to compensate for the latent heat of the vapor in the column. The temperature at which it was necessary to use the column heater was around 150° C. The column heater was started at a low amperage by using rheostatic control and the heat was gradually increased to facilitate maintenance of constant rate of condensate flow.

Distillation was continued until there was no liquid remaining in the distillation flask. At that time the flask and column heaters were turned off and any liquid distilling after that time was added to the residue in the flask. That residue was the result of condensation of the contents of the rectifying column.

Specific gravity was determined for each seven milliliter sample using the pycnometer method. Refractive indices were also recorded for these samples, using an Abbe' refractometer, and these data were determined at 20° C. to facilitate comparing results with the technical information available.

As a result of correlating data from fractional distillation of light crudes, the samples were placed in one of three groups, according to boiling point; group one (chiefly Laksol, or wood naphtha)- 69-151° C.; group two (chiefly turpentine)- 155-182° C.; and group three (some dipentene, the remainder pine oil)- 187-261° C.

Groups two and three were fractionated separately using the same procedure as was used in the fractionation of light crudes. Six milliliter samples were collected and the rate of condensate flow was approximately two milliliters per minute. Upon correlation of data obtained from the distillation of groups two and three, the following groups were established: Laksol, or wood naphtha,- 69-153° C.; dipentene- 169-190° C.; and pine oil- 200-247° C.

Specific gravity and refractive index determinations were made on each sample of each group and on each recombined group.

The plan and specifications for the fractional distillation apparatus may be found on page 91, Drawing No. 3, *Plan of a Laboratory Fractionation Column.*

**Chemical Processing.** In the course of chemical processing, five general reactions were investigated as to: (a) materials used, (b) conditions employed, and (c) general procedure. The reactions examined were: formation of

terpineol from pinene, terpin hydrate from pinene, dipentene from pinene, terpin hydrate from dipentene, and terpineol from dipentene. The investigations were made with the purpose that the best yields would be used for commercial production in the plant.

Formation of Terpineol from Pinene. Three general methods were examined for producing terpineol from pinene. The first consisted of dissolving pinene in glacial acetic acid and add to this solution sulfuric acid (98 per cent). The entire mixture was then added to distilled water. The resulting mixture was refluxed; at the end of which operation the top layer of the mixture was removed and distilled, the portion boiling at 200-214° C. (760 mm. Hg) being collected as terpineol. The second method investigated consisted of dissolving pinene in ethyl alcohol (95 per cent), dissolving sulfuric acid (98 per cent) in the solution, and adding the resulting mixture to distilled water. The mixture was then allowed to settle after thorough mixing. After settling, the top layer was removed and distilled, the portion boiling at 200-214° C. being collected as terpineol. The third method consisted of dissolving benzene sulfonic acid and an equivalent amount of pinene in glacial acetic acid and refluxing the mixture. At the end of reflux the top layer was removed and distilled, the portion boiling at

200-214° C. being collected as terpineol. Each of the above reactions was examined on the "best yield" basis by varying the conditions of time, temperature, and concentration.

Formation of Terpin Hydrate from Pinene. Two general methods were examined for producing terpin hydrate from pinene. The first method consisted of dissolving pinene in ethyl alcohol (95 per cent) and adding hydrochloric acid (sp. gr.1.16). The mixture was allowed to stand, then added to a large quantity of water, and later filtered to remove terpin hydrate crystals. The second method required essentially the same procedure as the first, with the exception of using sulfuric acid (98 per cent) instead of hydrochloric acid. Each of the above reactions was varied as to time, temperature, and concentration to determine the conditions giving the best yield.

Formation of Dipentene from Pinene. The method of producing dipentene from pinene was as follows: a measured amount of pinene was charged into an autoclave and heated. The vapor cock on the autoclave remained open until pinene vapors issued from the cock. At that time the cock was closed and at every ten degree interval above 150° C. the following data were recorded: pressure in the autoclave, time from start at that temperature, and refractive index

of a sample removed from the autoclave. The temperature was chosen which gave the best yield of dipentene, as determined by refractive index, and the above procedure was carried out except that no samples were removed at the ten degree temperature intervals. Upon reaching that optimum temperature, the vapor cock was opened and the dipentene was collected.

The plan and specifications of the autoclave may be found on page ///, Drawing No. 4.

Formation of Terpin Hydrate from Dipentene. The methods of producing terpin hydrate from dipentene was as follows: dipentene was allowed to stand with dilute sulfuric acid after thorough stirring; dipentene was refluxed with dilute sulfuric acid; and dipentene was refluxed with benzene sulfonic acid. At the end of each of the above reactions, the terpene layer was separated from the aqueous portion and distilled, the portion boiling at 200-214° C. being collected as terpineol. Each method was examined on the "best yield" basis.

Formation of Terpineol from Dipentene. The two methods for producing terpineol from dipentene were as follows: dipentene was dissolved in benzene sulfonic acid and glacial acetic acid and refluxed; and dipentene was added to sulfuric acid and dilute acetic acid and refluxed. In both cases

the top layer was removed and distilled, the portion boiling at 200-214° C. being collected as terpineol. Both reactions were examined as to best yield of terpineol due to variance of time, temperature, and concentration.

Plant Design and Location. On the basis of all experimental work and data obtained, a plant was designed to produce 100 pounds of terpineol per day. Equipment was selected that would be used in the plant. Using recorded data and making necessary calculations, material and heat balances were made across each piece of selected equipment. From these balances the equipment was designed as to size (14)(18) (44)(53)(89)(95), location in the plant, and on-stream operation (54). Each alternate method of producing the final product, terpineol, and side products by chemical processing was investigated as to equipment necessary and economics involved. The cost of buying, installing, and operating the equipment and maintaining the plant was calculated (101-105)

The location of the plant was selected upon consideration of the factors of raw materials source and supply, availability of market, transportation facilities, labor market, plant requirements, and source and availability of power (106)

Table I  
Data and Results

Destructive Distillation of Pine Wood Wastes

Run A-1

Date - February 6, 1947  
 Atmospheric temperature - 22.5° C.  
 Atmospheric pressure - 706.8 mm. Hg, abs.  
 Weight of pine wood used - 2218.8 grams  
 Size of pine wood - 4" long x ½" dia.  
 Time of start - 1330

Time	Temperatures					Weight	Volume	Volume
	Retort	Vapors	Cooling	Water	Conden-			
	°C.	°C.	In	Out	sate	ing	den-	cond.
hr.,	°C.	°C.	°C.	°C.	°C.	kg./	ml./	ml./
min.						min.	10 min.	sec.
0-00	22.5	20.5	9.5	9.5	--	2.772	--	--
10	37.9	25.0	9.5	9.5	--	2.772	--	--
20	143.5	30.0	10.0	10.0	--	2.788	--	--
30	205.0	51.5	10.0	10.0	--	2.744	--	--
40	246.5	105.0	10.0	10.0	10.0	2.792	--	36.1
50	279.5	145.0	10.0	10.0	16.0	2.744	38.0	23.2
1-00	260.0	130.0	10.0	10.2	16.0	2.528	45.5	4.78
10	232.5	100.0	10.0	10.0	18.0	2.800	17.0	4.34
20	251.5	95.5	10.0	10.0	20.0	2.548	9.5	--
30	232.5	91.0	10.0	10.0	21.0	2.620	7.0	--
40	238.0	92.0	10.0	10.0	21.0	2.544	6.0	--
50	240.5	93.5	10.0	10.0	21.0	0.927	9.0	--
2-00	237.0	94.0	10.0	10.7	21.0	0.915	9.0	0.99
10	249.0	95.0	10.0	10.9	20.0	0.875	10.0	--
20	251.5	95.0	10.0	11.0	19.5	0.831	14.0	2.54
30	255.0	95.0	10.0	11.1	19.5	0.801	13.5	--
40	255.0	96.0	10.0	11.4	19.5	0.774	15.0	--
50	261.2	98.5	10.0	11.7	19.0	0.795	18.0	--
3-00	244.5	95.0	10.0	11.5	19.0	0.735	10.0	2.56
10	262.5	95.0	10.0	11.8	19.0	0.714	11.5	--
20	266.3	95.0	10.0	11.8	19.0	0.747	12.0	--
30	244.5	94.0	10.0	11.5	20.0	0.747	9.0	--
40	250.0	91.0	10.0	11.5	20.0	0.777	5.0	--
50	266.0	92.0	10.0	11.6	20.0	0.747	4.5	--

Destructive Distillation of Pine Wood Wastes

Run A-1 (cont.)

Time hr.,	Temperatures					Weight Cool- ing Water kg./ min.	Volume Con- den- sate ml./ 10 min.	Volume Non- cond. Vapors ml./ sec.
	Retort °C.	Vapors °C.	Cooling In °C.	Water Out °C.	Conden- sate °C.			
4-00	283.0	97.0	10.0	12.0	19.5	0.774	10.0	10.83
10	292.5	104.0	10.0	12.3	19.0	0.754	14.0	--
20	306.5	108.5	10.0	12.5	19.0	0.771	11.5	--
30	319.0	122.0	10.0	12.8	19.0	0.711	21.0	18.56
40	352.0	193.0	10.0	14.0	18.0	0.741	40.0	--
50	358.5	224.5	10.0	15.0	18.0	0.697	57.0	--
5-00	371.7	222.0	10.0	13.5	18.0	0.727	40.0	21.65
10	377.0	194.0	10.0	13.0	18.0	0.712	32.0	--
20	407.5	217.0	10.0	14.5	18.0	0.682	23.0	--
30	432.0	239.0	10.0	15.2	18.5	0.703	30.0	81.3
40*	452.5	259.0	10.0	14.5	18.5	0.703	33.0	--
45	462.0	254.0	10.0	14.0	18.5	0.693	--	--
50	435.0	222.0	10.0	13.2	17.5	0.712	23.0	--
55	413.0	177.0	10.0	13.5	17.5	0.732	--	--
6-00	399.5	157.0	10.0	12.0	17.5	0.711	11.5	--
05	371.7	128.0	10.0	11.9	17.5	0.756	--	--
10	349.0	108.0	10.0	11.9	17.5	0.681	3.5	--
15	331.0	96.0	10.0	10.0	--	0.703	negl.	--
30	260.0	71.0	10.0	10.0	--	0.742	--	--

\* Denotes time of burner cut-off in furnace

Products of Destructive Distillation

<u>Product</u>	<u>Description</u>	<u>Amount</u>	<u>Density</u>
Top Layer	black	117.5 ml.	0.978 gms./ml.
Bottom Layer	amber-colored	420.0 ml.	0.944 gms./ml.
Charcoal	black	873 gms.	0.6 gms./ml. (c.)

## Results of Destructive Distillation

### Graphs 1 and 2

The results of Run A-1, as tabulated in Graphs 1 and 2, Vapor and Retort Temperatures vs. Time, and Condensate and Vapor Rates vs. Time, respectively, indicate the following:

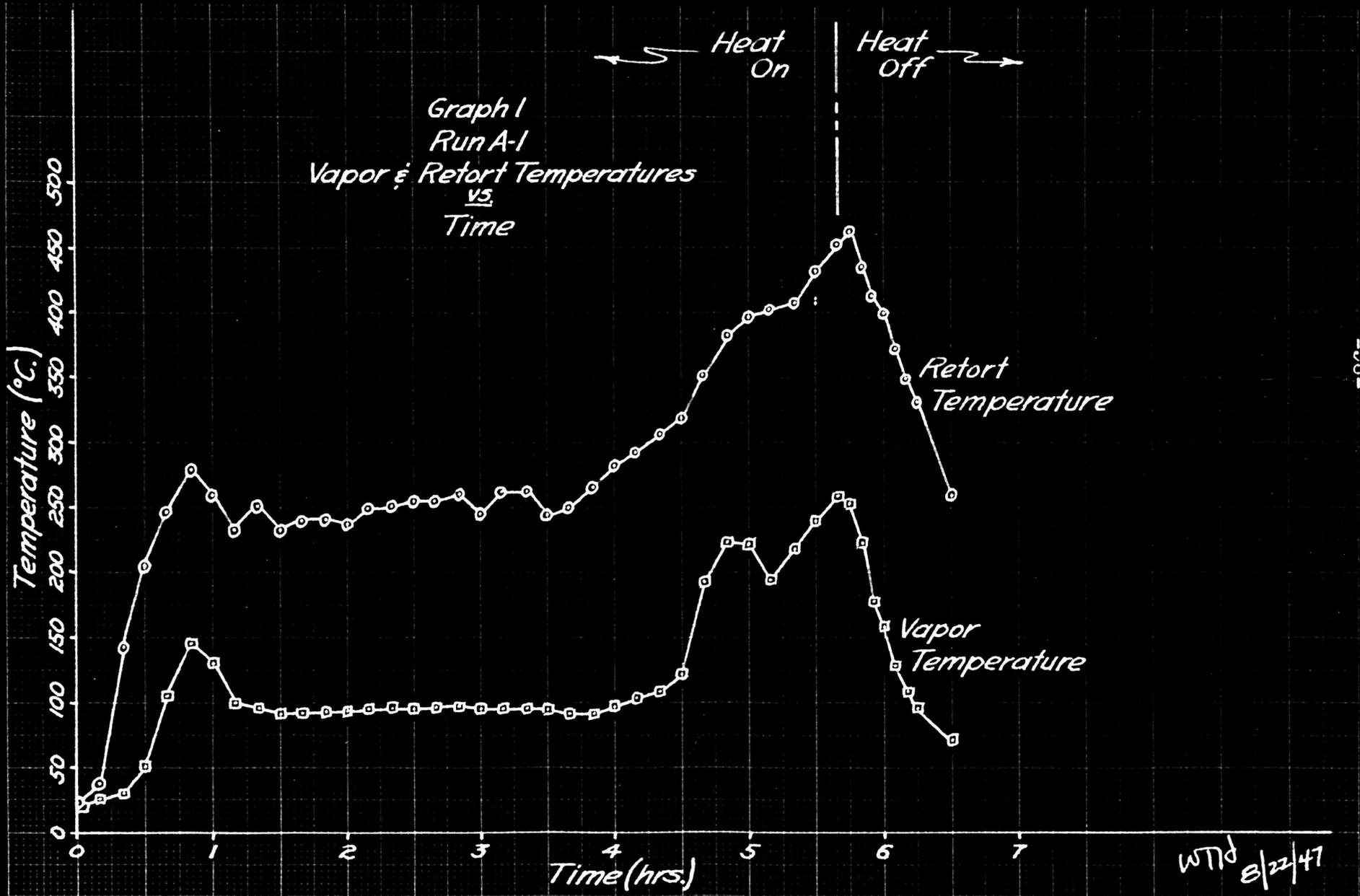
1) The temperature of the vapors leaving the retort lags behind the temperature of the retort.

2) The temperatures of the retort and of the vapor leaving the retort drop quickly after the burner in the furnace is cut off.

3) The vapor and condensate rates follow the same general path, one closely preceding or following the other rate.

4) The vapor and condensate rates drop off quickly after the burner in the furnace is cut off.

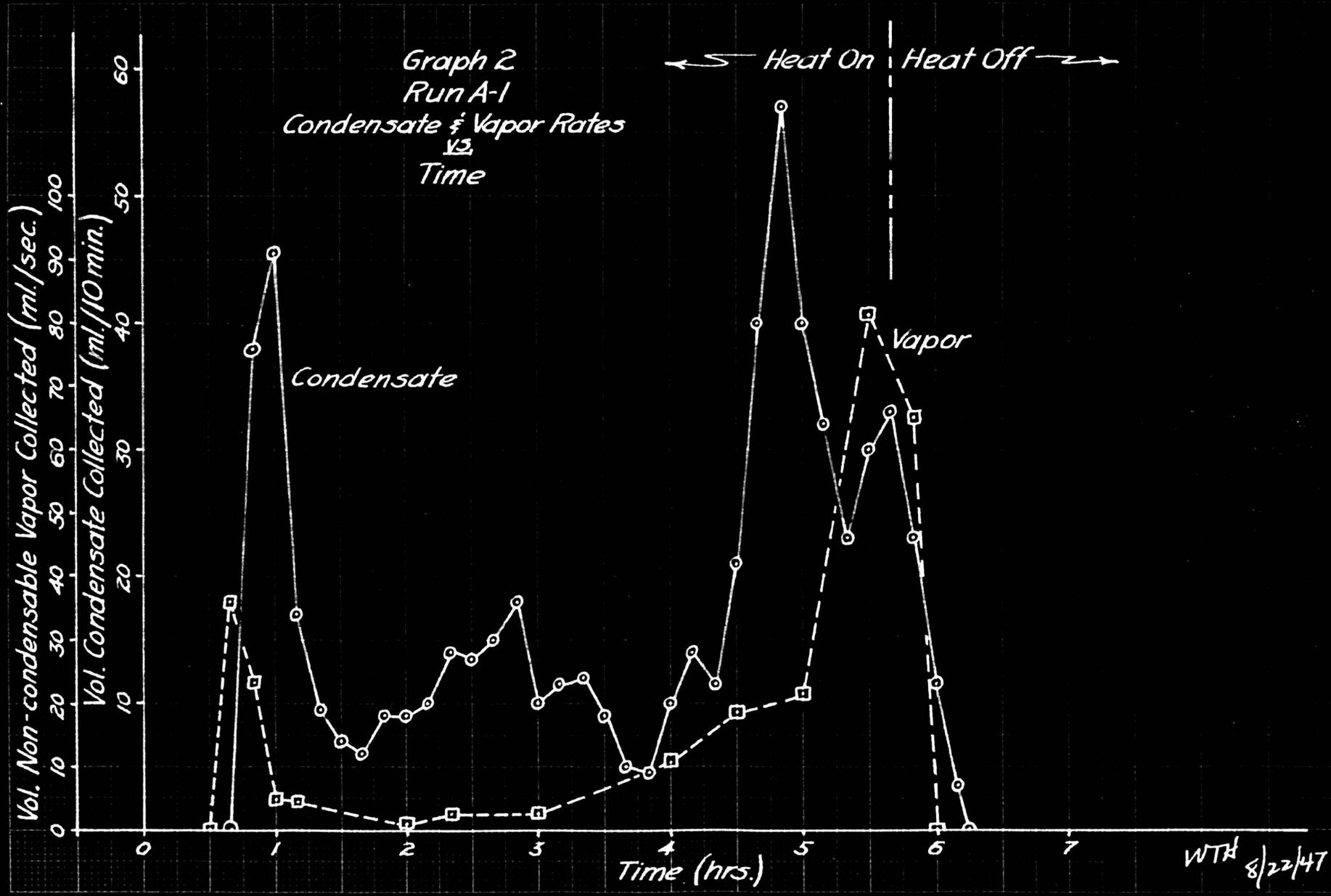
5) The vapor and condensate rates vary as the retort and vapor temperatures, the former being an exaggeration in change of the latter.



WTD 8/22/47

Graph 2  
Run A-1  
Condensate & Vapor Rates  
vs.  
Time

← Heat On | Heat Off →



WTH 8/22/47

Table II

Destructive Distillation of Pine Wood Wastes

Run A-2

Date - February 25, 1947  
 Atmospheric temperature - 23.5° C.  
 Atmospheric pressure - 725.8 mm. Hg, abs.  
 Weight of pine wood used - 1625 grams  
 Size of pine wood - 5" long x 1/2" dia.  
 Time of start - 1100

Time	Temperatures					Weight	Volume	Volume
	Retort	Vapors	Cooling	Water	Conden-			
hr., min.	°C.	°C.	°C.	°C.	°C.	kg./ min.	ml./ 10 min.	ml./ sec.
0-00	22.5	22.5	10.0	10.0	--	0.674	--	--
10	51.6	24.5	10.0	10.0	--	0.654	--	--
20	116.5	27.0	10.0	10.0	--	0.646	--	--
30	156.0	28.0	10.5	11.0	--	0.660	--	--
40	177.0	28.0	10.5	11.0	--	0.675	--	--
50	191.0	28.5	10.5	11.0	--	0.650	--	--
1-00	196.0	30.0	10.5	11.0	--	0.644	--	--
10	221.5	41.5	11.0	11.5	--	0.610	--	6.1
20	246.5	71.0	11.0	11.8	--	0.580	--	7.0
30	246.5	83.0	11.0	12.0	--	0.560	--	3.8
40	244.5	88.5	11.0	12.0	--	0.586	--	3.8
50	254.0	92.0	11.0	12.0	20.0	0.580	5	3.5
2-00	257.0	93.0	11.0	12.0	19.0	0.550	10	3.8
10	262.0	94.5	11.0	12.2	18.5	0.560	15	6.3
20	279.5	97.0	11.0	13.0	17.5	0.590	22	6.6
30	276.0	97.0	11.0	12.7	17.0	0.590	26	6.0
40	278.5	98.0	11.0	12.9	17.5	0.550	22	5.5
50	278.5	97.5	11.0	12.3	18.0	0.560	18	5.1
3-00	286.0	98.5	11.0	12.3	18.5	0.580	17	5.5
10	288.0	99.5	11.0	13.0	18.0	0.560	17	6.3
20	295.5	103.0	11.0	13.0	18.0	0.520	19	7.3
30	295.0	103.5	11.0	12.5	17.5	0.550	19	6.0
40	295.0	101.0	11.0	12.6	18.5	0.590	14	5.7
50	296.5	100.0	11.0	12.5	18.0	0.526	15	6.3
4-00	302.5	103.0	11.0	13.0	18.5	0.530	14	7.7
10	306.5	103.0	11.0	13.1	18.0	0.520	15	8.8
20	316.5	106.5	11.0	13.4	18.0	0.500	16	10.1
30	316.5	103.0	11.0	13.2	18.2	0.470	14	8.8

Destructive Distillation of Pine Wood Wastes

Run A-2 (cont.)

Time	Temperatures					Weight	Volume	Volume
	Retort	Vapors	Cooling	Water	Conden-			
hr., min.	°C.	°C.	°C.	°C.	°C.	kg./ min.	ml./ 10 min.	ml./ sec.
4-40	321.5	103.0	11.0	13.2	19.0	0.520	13	11.0
50	332.0	107.0	11.4	13.5	18.5	0.506	12	14.7
5-00	340.0	110.5	11.8	13.7	18.0	0.500	13	14.7
10	339.0	105.0	11.8	13.2	18.0	0.470	13	12.0
20	336.0	110.0	12.0	13.4	18.5	0.480	10	8.2
30	341.0	97.0	12.0	13.3	21.0	0.470	8	8.8
40	346.5	97.0	12.0	13.7	20.5	0.460	8	13.2
50	366.0	109.0	12.0	14.0	18.0	0.480	10	24.4
6-00	380.0	122.0	11.8	13.8	18.5	0.500	15	27.5
10	397.0	140.0	11.8	14.2	18.0	0.480	13	24.4
20	401.0	147.5	12.3	14.4	18.0	0.510	20	33.0
30	407.5	141.0	12.4	14.5	19.0	0.480	16	33.0
40	427.0	143.0	12.5	14.5	19.0	0.470	14	35.0
50	438.0	145.0	12.5	14.5	19.0	0.466	12	33.9
7-00*	467.0	154.0	12.5	15.0	19.0	0.480	16	38.9
05	475.0	162.0	12.5	15.0	--	--	--	--
10	467.0	155.0	12.5	15.0	19.0	0.460	12	33.0
15	432.0	141.5	12.4	14.0	--	--	--	14.5
20	394.0	118.0	12.4	13.8	14.0	0.460	11	6.0
25	371.7	103.0	12.2	12.8	--	0.484	--	--
30	355.0	94.0	12.2	12.6	14.0	0.472	3	--
45	299.5	94.0	--	--	--	--	--	--

\* Denotes time of burner cut-off in furnace

Products of Destructive Distillation

<u>Product</u>	<u>Description</u>	<u>Amount</u>	<u>Density</u>
Top Layer	black	114 ml.	0.963 gms./ml.
Bottom Layer	amber-colored	306 ml.	0.989 gms./ml.
Charcoal	black	690 gms.	0.6 gms./ml. (c.)

## Results of Destructive Distillation

### Graphs 3 and 4

The results of Run A-1, as tabulated in Graphs 3 and 4, Vapor and Retort Temperatures vs. Time, and Condensate and Vapor Rates vs. Time, respectively, indicate the following:

1) The temperature of the vapors leaving the retort lags behind the retort temperature.

2) The temperatures of the retort and of the vapors leaving the retort drop quickly after the burner in the furnace is cut off.

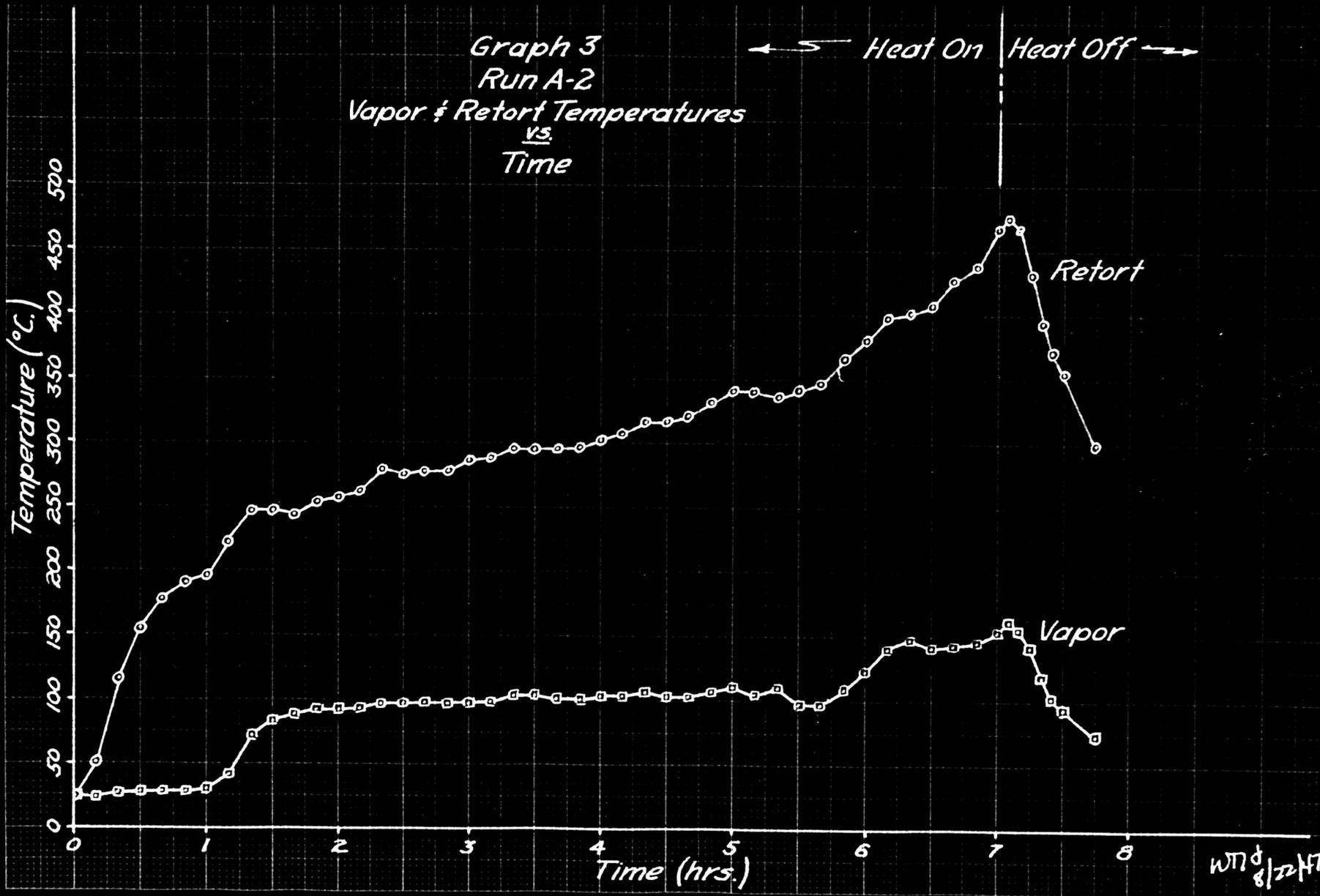
3) The vapor and condensate rates follow the same general path, one closely preceding or following the other.

4) The vapor and condensate rates drop off quickly after the burner in the furnace is cut off.

5) The vapor and condensate rates vary as the retort and vapor temperatures, the former being an exaggeration in change of the other.

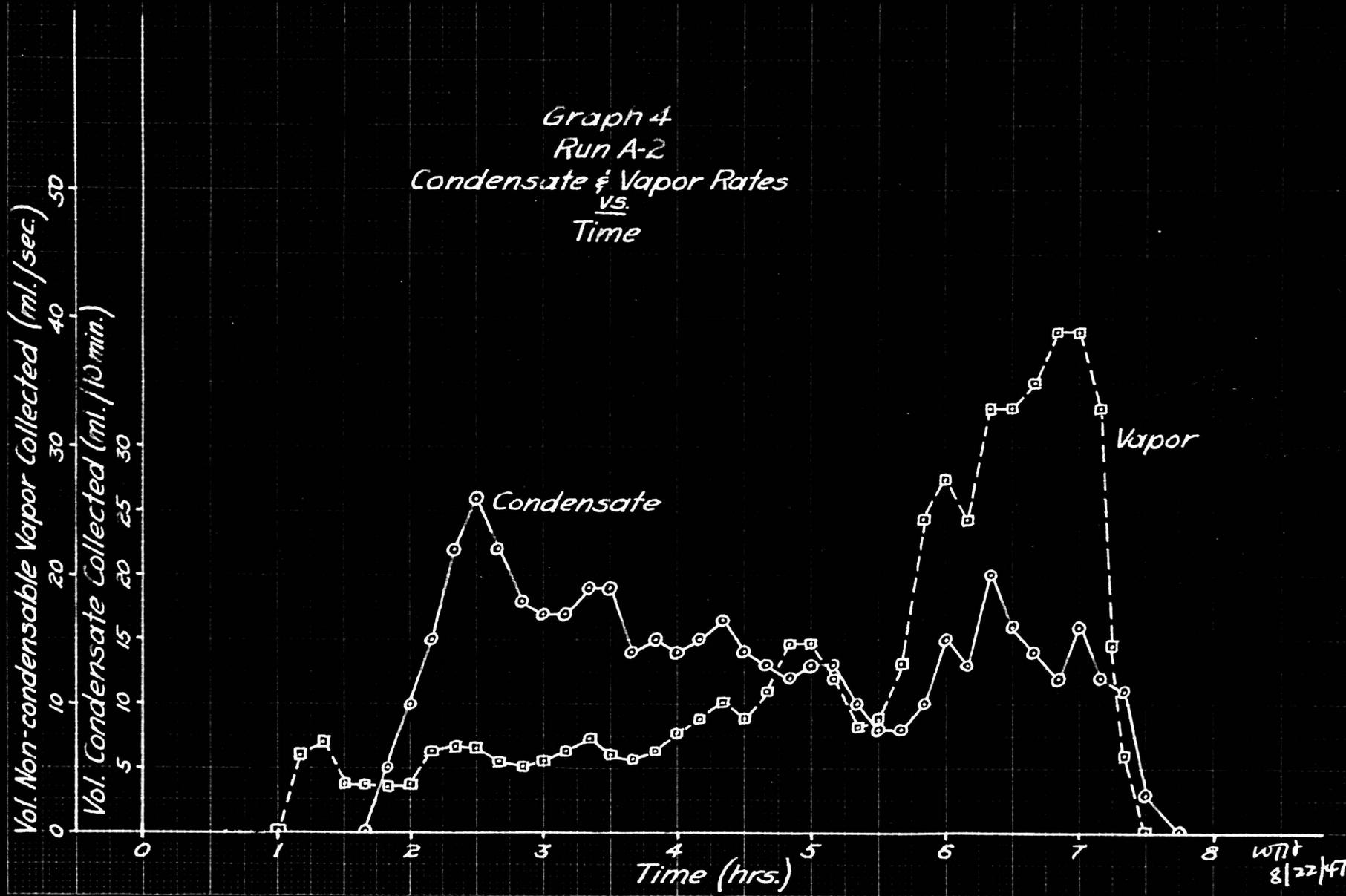
Graph 3  
Run A-2  
Vapor & Retort Temperatures  
vs  
Time

← Heat On Heat Off →



WTD  
8/22/47

Graph 4  
Run A-2  
Condensate & Vapor Rates  
vs.  
Time



WTT  
8/22/47

Table III

Destructive Distillation of Pine Wood Wastes

Run A-3

Date - March 14, 1947  
 Atmospheric temperature - 24.5° C.  
 Atmospheric pressure - 728.7 mm. Hg, abs.  
 Weight of pine wood used - 3900 grams  
 Size of pine wood - 4" long x ½" dia.  
 Time of start - 1515

Time hr., min.	Temperatures					Weight Cool- ing Water kg./ min.	Volume Con- den- sate ml./ 10 min.	Volume Non- cond. Vapors ml./ sec.
	Retort °C	Vapors °C.	Cooling In °C.	Water Out °C.	Conden- sate °C.			
0-00	24.5	24.5	10.5	10.5	--	1.070	--	--
15	96.0	24.0	11.0	11.0	--	1.009	--	--
30	143.5	25.0	11.2	11.5	--	1.029	--	--
45	191.0	28.5	11.2	11.5	--	0.984	--	--
1-00	260.0	89.0	11.0	12.2	18.0	1.012	12.0	22.5
15	306.5	176.0	11.0	17.0	17.0	0.969	134.0	27.5
30	318.0	203.5	11.2	16.0	17.0	0.984	132.0	44.0
45*	415.5	245.0	11.2	15.8	18.0	1.012	230.0	132.0
2-00	343.5	163.0	11.2	12.0	18.0	1.025	43.0	16.2
15	294.0	103.5	11.2	11.8	18.0	0.999	11.0	--
30	243.0	72.5	11.2	11.7	18.0	1.029	4.0	--

\* Denotes time of burner cut-off in furnace.

Products of Destructive Distillation

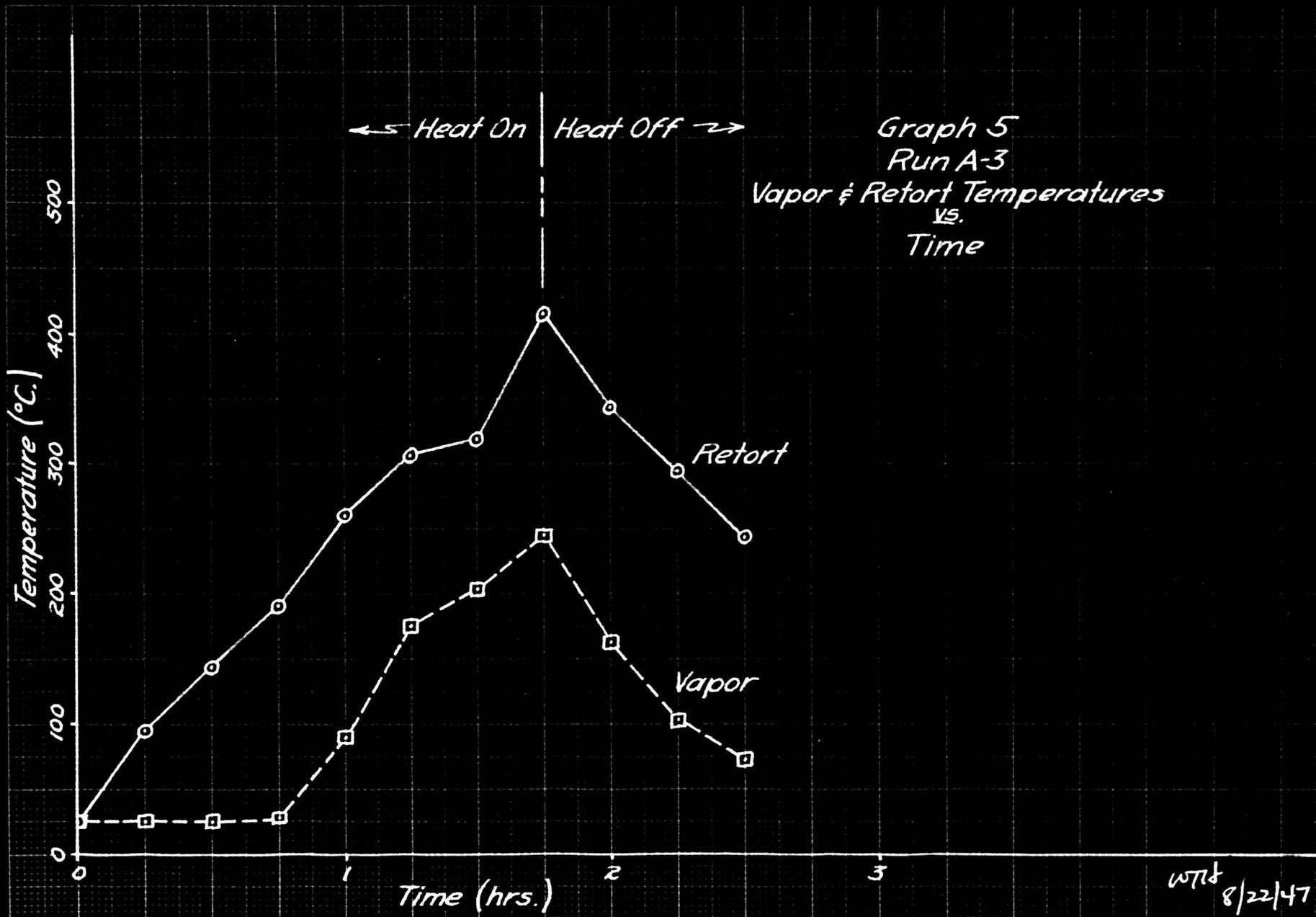
<u>Product</u>	<u>Description</u>	<u>Amount</u>	<u>Density</u>
Top Layer	black	264 ml.	0.930 gms./ml.
Bottom Layer	amber-colored	297 ml.	1.011 gms./ml.
Creosote	black	153 gms.	1.229 gms./ml.
Charcoal	black	1254 gms.	0.6 gms./ml. (c.)

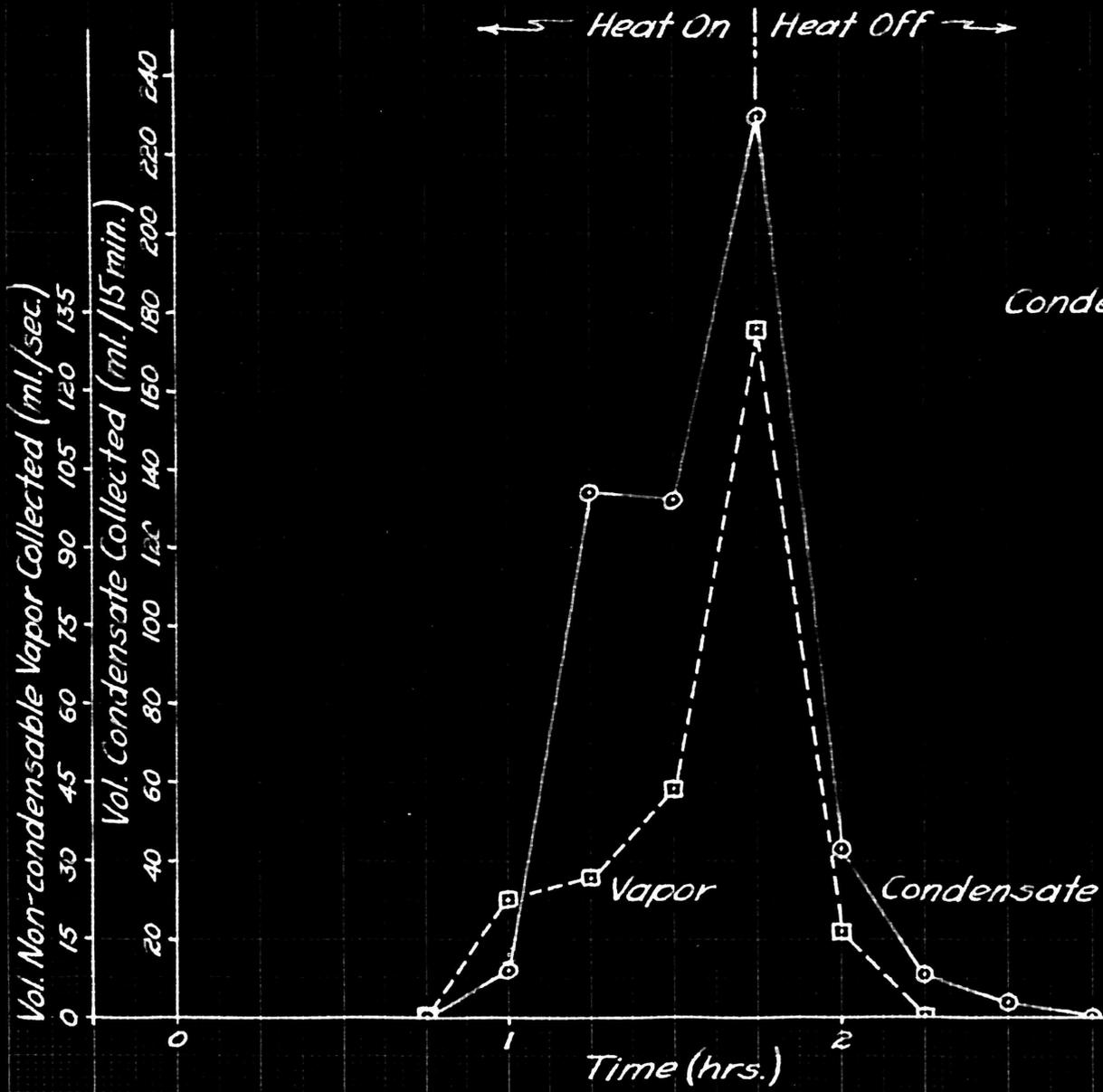
## Results of Destructive Distillation

### Graphs 5 and 6

The results of Run A-3, as tabulated in Graphs 5 and 6, Vapor and Retort Temperatures vs. Time, and condensate and Vapor Rates vs. Time, respectively, indicate the following:

- 1) The temperature of the vapors leaving the retort lags behind the temperature of the retort.
- 2) The temperatures of the retort and of the vapor leaving the retort drop quickly after the burner in the furnace is cut off.
- 3) The vapor and condensate rates follow the same general path, one closely preceding or following the other rate.
- 4) The vapor and condensate rates drop off quickly after the burner in the furnace is cut off.
- 5) The vapor and condensate rates vary as the retort and vapor temperatures, the former being an exaggeration in change of the latter.





Graph 6  
Run A-3  
Condensate & Vapor Rates  
vs.  
Time

WTT 8/22/47

Destructive Distillation of Pine Wood Wastes

Non-Condensable Vapors

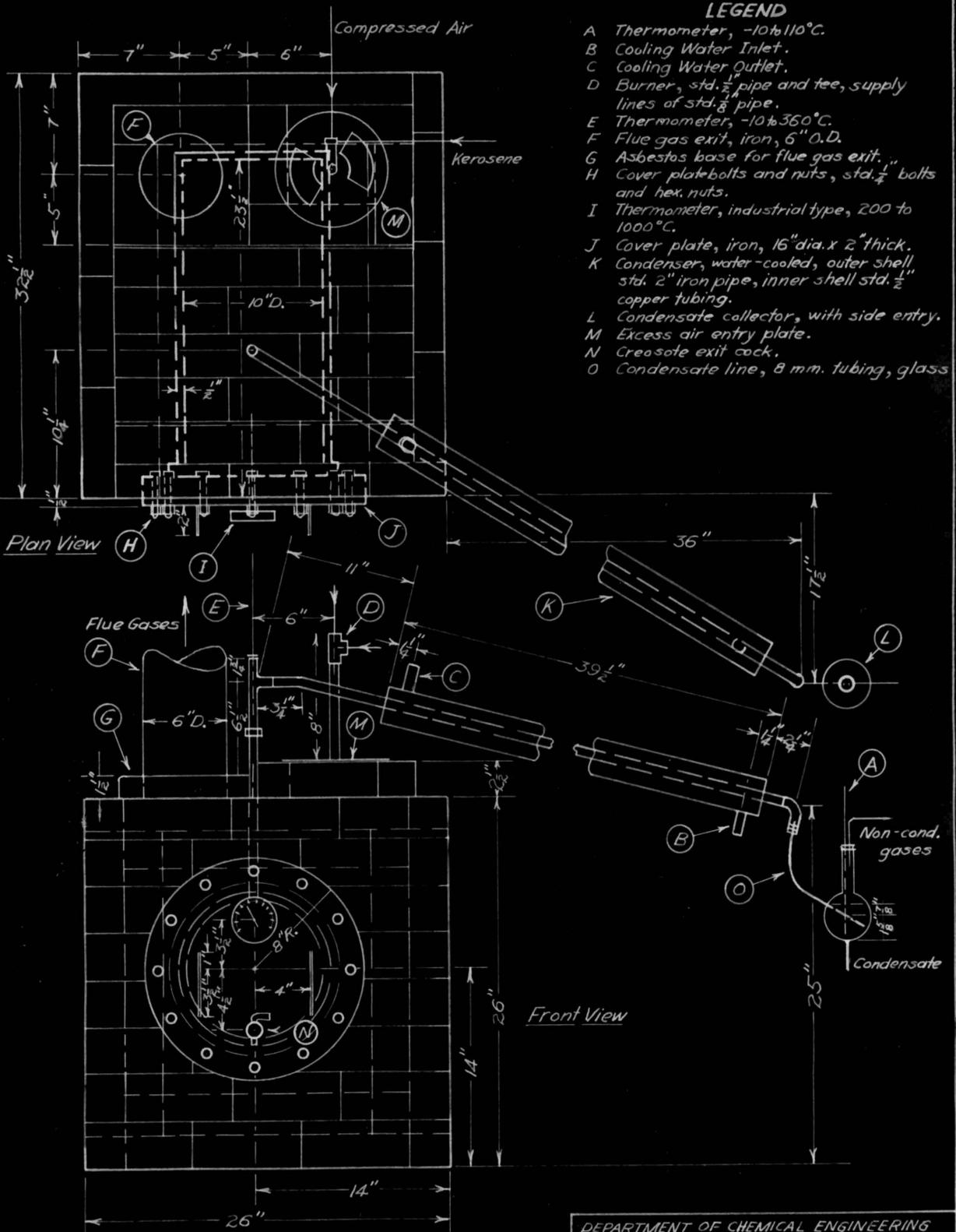
The following data are the calculated areas under the Vapor Rate vs. Time curves in Graphs 2, 4, and 6, Condensate and Vapor Rates vs. Time:

Run A-1	339,185 ml. vapor
Run A-2	304,160 ml.
Run A-3	<u>206,300</u> ml.
	849,645 ml. non-condensable vapors

The density of the non-condensable vapors was as follows:

Calculated	$3.84 \times 10^{-3}$ gms./ml.
Experimental	$3.05 \times 10^{-3}$ gms./ml.

The heat value of the non-condensable vapors was assumed to be 100 Btu/cu. ft. (8)(51) .



**LEGEND**

- A Thermometer, -10 to 110°C.
- B Cooling Water Inlet.
- C Cooling Water Outlet.
- D Burner, std. 1/2" pipe and tee, supply lines of std. 3/8" pipe.
- E Thermometer, -10 to 360°C.
- F Flue gas exit, iron, 6" O.D.
- G Asbestos base for flue gas exit.
- H Cover plate bolts and nuts, std. 1/4" bolts and hex nuts.
- I Thermometer, industrial type, 200 to 1000°C.
- J Cover plate, iron, 16" dia. x 2" thick.
- K Condenser, water-cooled, outer shell std. 2" iron pipe, inner shell std. 1/2" copper tubing.
- L Condensate collector, with side entry.
- M Excess air entry plate.
- N Creosote exit cock.
- O Condensate line, 8 mm. tubing, glass

**NOTES**

All outer walls of furnace are common red brick, 7 3/4" x 3 3/4" x 2 1/4". All inner walls are fire brick, 8 1/2" x 4" x 2 1/4".  
 Glassware is "Pyrex" brand, std. thickness.  
 Condensate line is 3/8" copper tubing.

DEPARTMENT OF CHEMICAL ENGINEERING  
 VIRGINIA POLYTECHNIC INSTITUTE  
 BLACKSBURG, VIRGINIA

PLAN OF A  
 DESTRUCTIVE DISTILLATION FURNACE

SCALE: 1"=10"  
 DRAWN BY WJH DATE 6/27/47  
 CHECKED BY FCV DATE 7/2/47  
 APPRVD. BY FCV DATE 7/2/47

DWNG. NO. 1  
 CASE NO. 47  
 FILE NO. 539

Table IV

A. S. T. M. Distillation of Heavy Crudes  
 (bottom layer from composite destructive distillation  
 runs A-1, A-2, and A-3)

Date - April 1, 1947  
 Atmospheric temperature - 28.5° C.  
 Atmospheric pressure - 719.2 mm. Hg, abs.  
 Amount of charge - 750 ml.  
 Distillation rate - 5 ml. per min.  
 Time of start - 1510

Per Cent Distilled	Amount Distilled	Vapor Temperature	Density
%	%	°C.	gms./ml.
0	0	95.0	0.9981
10	75	103.5	0.9673
20	150	107.0	0.9792
30	225	116.0	0.9815
40	300	123.5	0.9826
50	375	133.0	0.9830
60	450	143.5	0.9837
70	525	163.0	0.9841
80	600	185.0	0.9849
90	675	231.0	0.9878
92	690	247.0	0.9947
94	705	249.0	1.0017
Res.	732	---	1.2794

Results of A. S. T. M. Distillation

Graph 7

As indicated by Graph 7, Per Cent Distilled vs. Boil-  
 ing Point, on the following page, the boiling point of the  
 avy crudes increases sharply with an inclination to reach  
 0 per cent at 100 per cent distilled.

Graph 7  
A.S.T.M. Distillation of Heavy Crudes  
Per Cent Distilled  
vs.  
Boiling Point

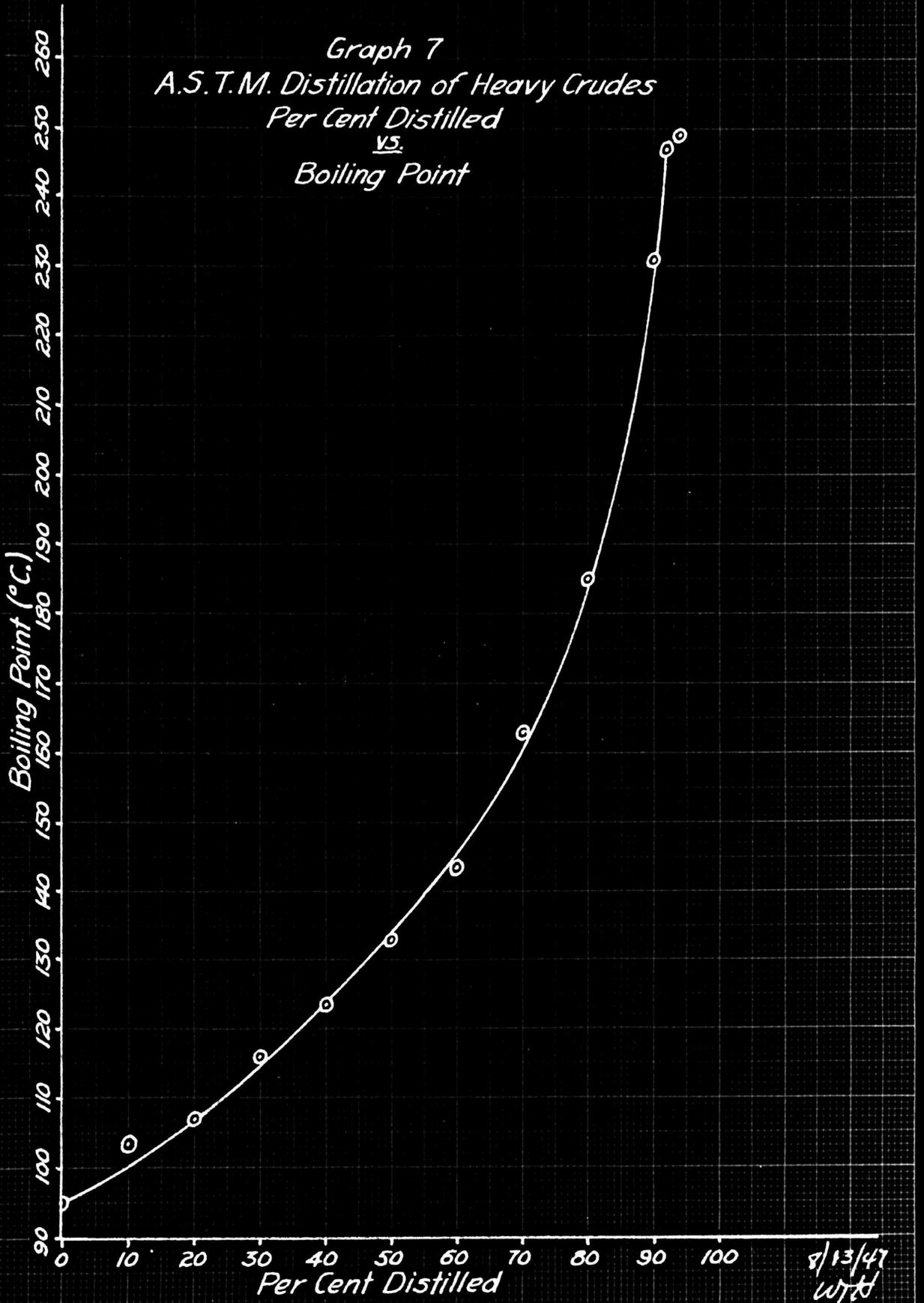


Table V

A. S. T. M. Distillation of Top Layer  
from Composite Destructive Distillation

Runs A-1, A-2, and A-3

Date - April 5, 1947  
Atmospheric temperature - 25.0° C.  
Atmospheric pressure - 714.8 mm. Hg, abs.  
Amount of charge - 472 ml.  
Distillation rate - 5 ml./min.  
Time of start - 1245

Per Cent Distilled	Amount Distilled	Vapor Temperature	Density
%	ml.	°C.	gms./ml.
0	0	94.0	0.9299
10	47	108.0	0.8185
			0.9725*
20	94	110.0	0.8330
			0.9762*
30	141	114.0	0.8373
			0.9797*
40	188	121.0	0.8403
			0.9810*
50	235	135.0	0.8420
			0.9836*
60	282	172.5	0.8529
			0.9920*
70	329	200.0	0.8911
80	376	241.0	0.9244
90	423	301.0	0.9870
94	440.5	310.0	1.0041
Res.	465	---	1.2290

\* Upon distillation of the top layer, the first 60 per cent of the condensate separated into two layers, with the bottom layer being pyroligneous licuor.



Table VI

Fractional Distillation of Light Crudes

Run F.D.-1

Date - April 27, 1947  
 Atmospheric temperature - 30.0° C.  
 Atmospheric pressure - 711.6 mm. Hg, abs.  
 Amount of charge - 254 ml.  
 Distillation rate - 7 ml./4 min.  
 Time of start - 1230  
 Time from start of first vapor - 0 hrs., 13 min., 30 sec.  
 Duration of total reflux - 5 min.  
 Flask temperature during total reflux - 102.0° C.

Bottle No.	Amount Distilled ml.	Temperatures Flask °C.	Vapors* °C.	Sp. Gr.**	$n_D^{20^\circ}$
--	0	108.0	46.0	--	--
1	7	120.0	69.1	0.8476	1.4520
2	14	138.0	78.1	0.8598	1.4639
3	21	169.0	107.2	0.8792	1.4723
4	28	173.0	132.3	0.8832	1.4732
5	35	175.5	137.3	0.8914	1.4748
6	42	177.0	146.3	0.8900	1.4787
7	49	180.0	146.3	0.8890	1.4790
8	56	183.0	151.4	0.8818	1.4794
9	63	184.0	155.4	0.8750	1.4794
10	70	187.0	155.4	0.8720	1.4794
11	77	188.0	160.5	0.8690	1.4792
12	84	191.0	162.5	0.8643	1.4797
13	91	194.0	168.5	0.8652	1.4803
14	98	195.0	166.5	0.8668	1.4812
15	105	199.0	166.5	0.8685	1.4818
16	112	205.0	168.5	0.8670	1.4826
17	119	206.0	171.5	0.8674	1.4837
18	126	208.0	173.6	0.8692	1.4857
19	133	210.0	174.6	0.8712	1.4874
20	140	212.0	176.6	0.8771	1.4903
21	147	217.0	177.7	0.8794	1.4910
22	154	224.0	182.6	0.8853	1.4940
23	161	234.0	187.5	0.9028	1.5020
24	168	242.0	199.7	0.9307	1.5126
25	175	249.0	208.7	0.9644	1.5207

\* Temperature corrected for thermometer stem and atmosphere.

\*\* Specific gravity corrected for temperature and pycnometer.

Fractional Distillation of Light Crudes

Run F.D.-1 (cont.)

Bottle No.	Amount Distilled ml.	Temperatures		Sp. Gr.	$n_D^{20^\circ}$
		Flask $^\circ\text{C.}$	Vapors $^\circ\text{C.}$		
26	182	257.0	212.7	0.9768	1.5242
27	189	262.0	220.8	0.9800	1.5268
28	196	278.0	231.8	0.9839	1.5320
29	203	303.0	255.0	0.9942	1.5397
30	205	308.0	264.0	--	1.5510

Correlation of Run F.D.-1

Bottle Nos.	Temperature Range	Specific Gravity Range	Refractive Index Range
	$^\circ\text{C.}$		$20^\circ\text{C.}$
1-8	69.1-151.4	0.8476-0.8818	1.4720-1.4794
9-22	155.4-182.6	0.8750-0.8853	1.4794-1.4940
23-30	187.5-264.0	0.9028-0.9942	1.5020-1.5510

## Results of Fractional Distillation

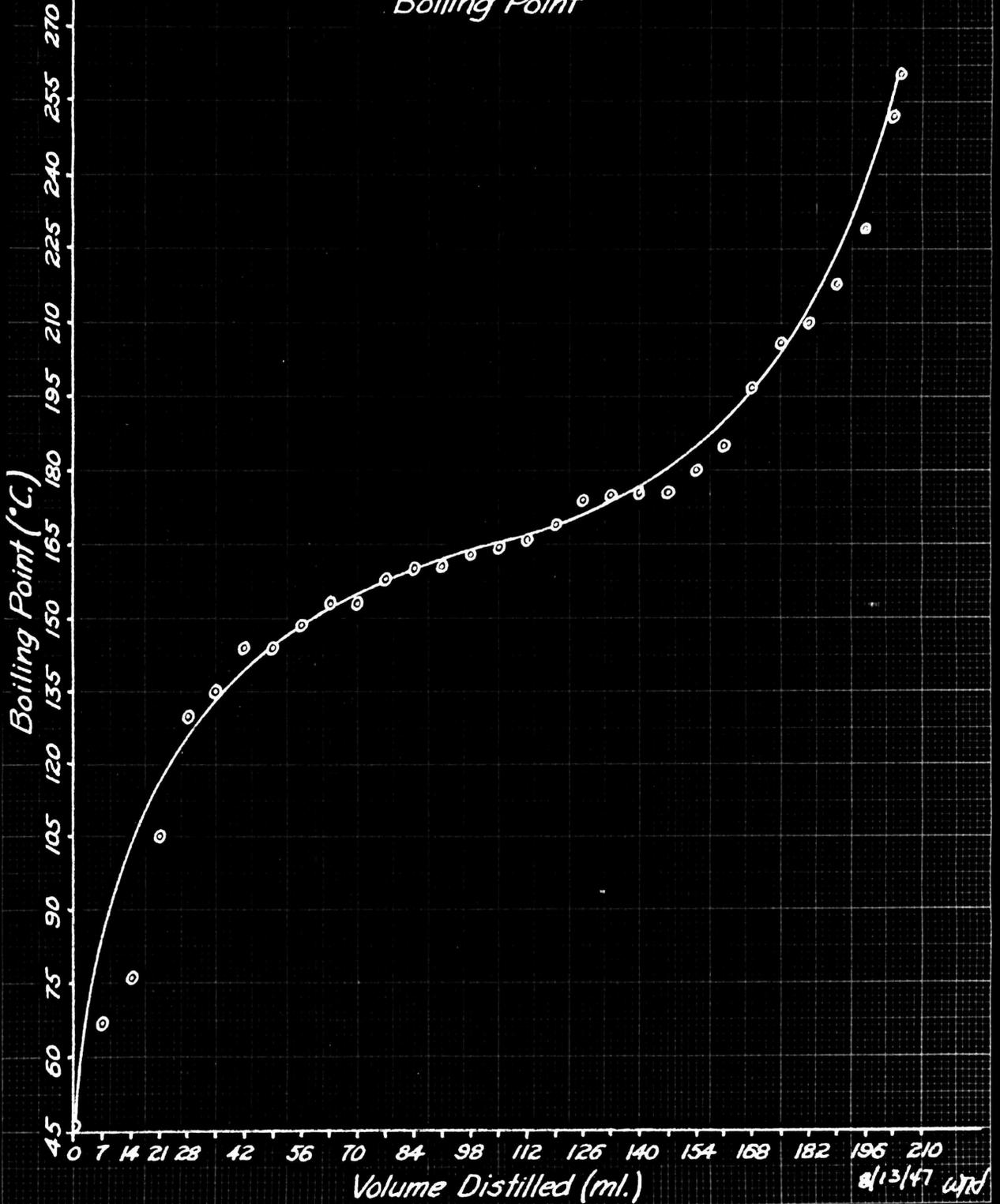
### Graphs 8, 9, and 10

Graph 8, Volume Distilled vs. Boiling Point, on the following page, is the true-boiling-point curve for the light crudes obtained from the A. S. T. M. Distillation of the Composite Destructive Distillation runs.

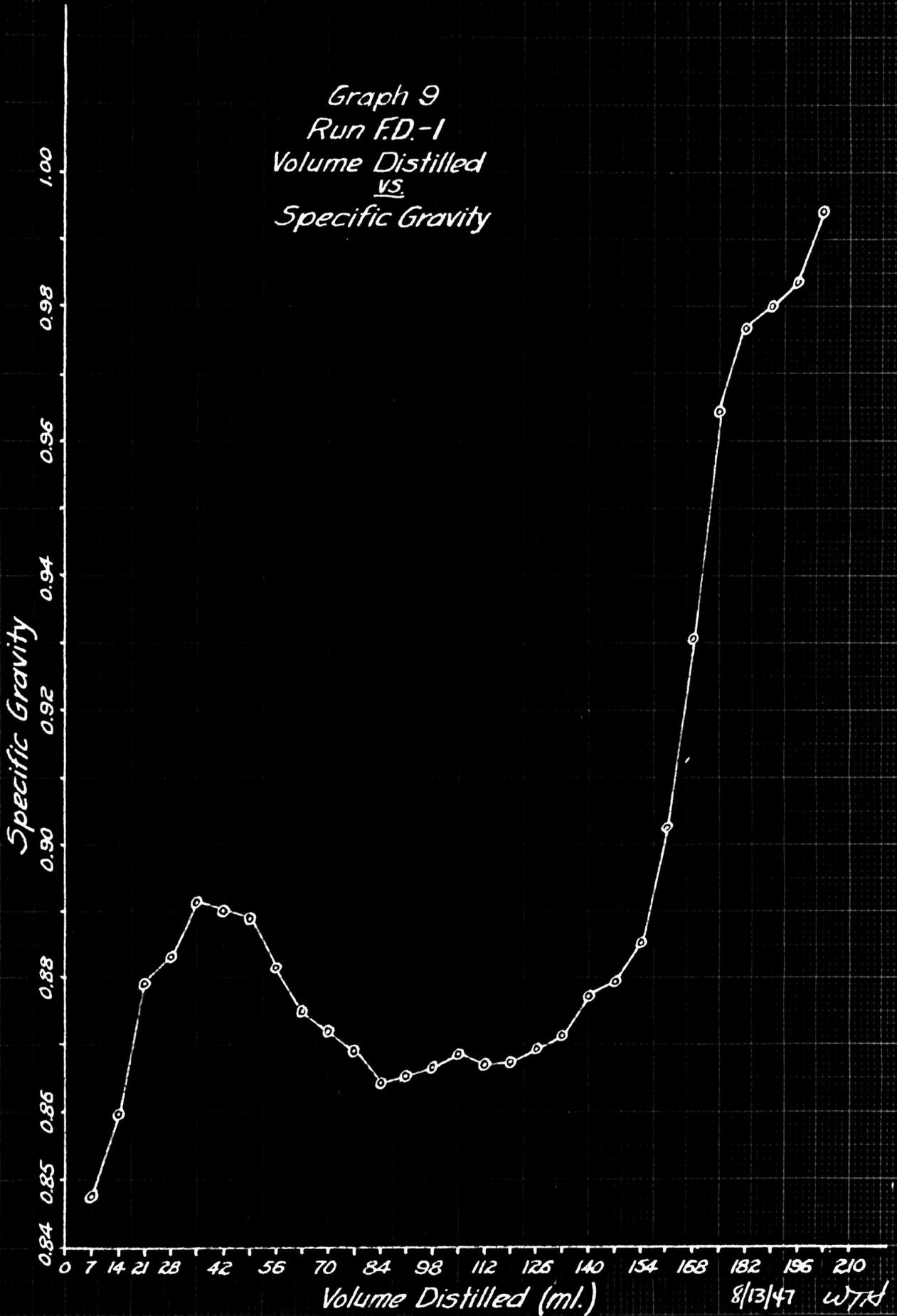
Graph 9, Volume Distilled vs. Specific Gravity, on the second page following, indicates the change in specific gravity due to fractional distillation, or increase in boiling point.

Graph 10, Volume Distilled vs. Refractive Index, on the third page following, indicates refractive index varying with the amount distilled, or the increase in boiling point.

Graph 8  
Run F.D. -1  
Volume Distilled  
vs.  
Boiling Point



Graph 9  
Run F.D.-1  
Volume Distilled  
vs.  
Specific Gravity



8/13/47 WTK

Graph 10  
Run F.D.-1  
Volume Distilled  
vs.  
Refractive Index

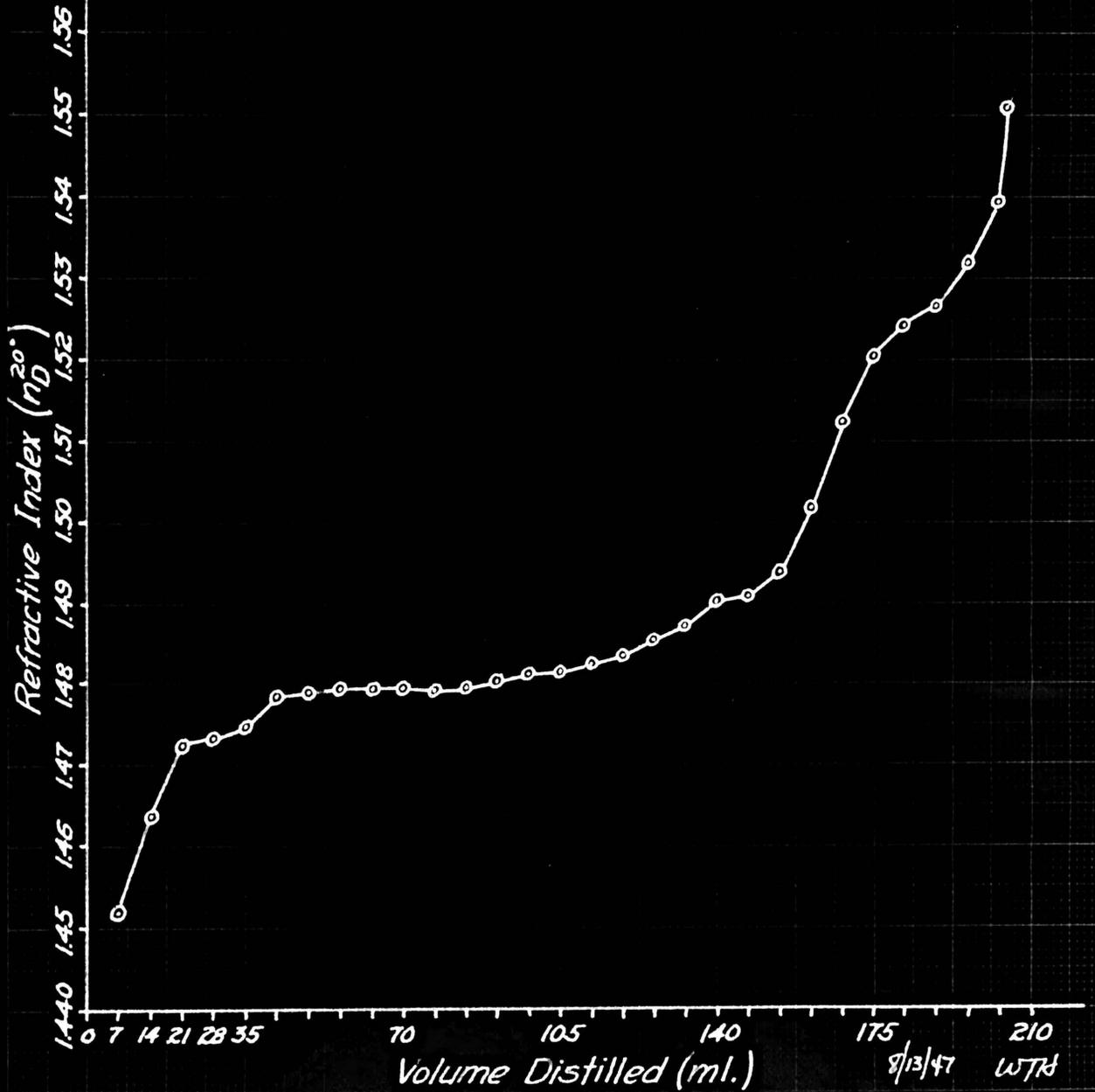


Table VII

Fractional Distillation of Middle Fraction (155°-182° C.)

of Run F.D.-1

Run F.D.-2

Date	- May 7, 1947
Atmospheric temperature	- 24.0° C.
Atmospheric pressure	- 709.5 mm. Hg, abs.
Amount of charge	- 86 ml.
Distillation rate	- 2 ml./min.
Time of start	- 1400
Time from start of first vapor	- 0 hrs., 14 min., 30 sec.
Duration of total reflux	- 5 min.
Flask temperature during total reflux	- 159° C.

Bottle No.	Amount Distilled ml.	Temperatures Flask °C.	Vapors* °C.	Sp. Gr.**	nd <sup>20°</sup>
--	0	164	137.3	--	--
1	6	166	156.4	0.8751	1.4798
2	12	169	157.4	0.8695	1.4802
3	18	171	161.5	0.8718	1.4802
4	24	173	161.5	0.8688	1.4810
5	30	174	165.0	0.8674	1.4810
6	36	174	165.0	0.8653	1.4817
7	42	176	166.0	0.8660	1.4823
8	48	178	168.5	0.8653	1.4831
9	54	192	169.0	0.8660	1.4830
10	60	197	169.5	0.8653	1.4835
11	66	195	172.1	0.8650	1.4840
12	72	187	174.6	0.8670	1.4860
13	78	195	177.6	0.8705	1.4884
14	84	190	191.1	0.8813	1.4940
15	85	195	192.7	--	1.5019

\* Temperature corrected for thermometer stem and atmosphere

\*\* Specific gravity corrected for temperature and pycnometer.

## Results of Fractional Distillation

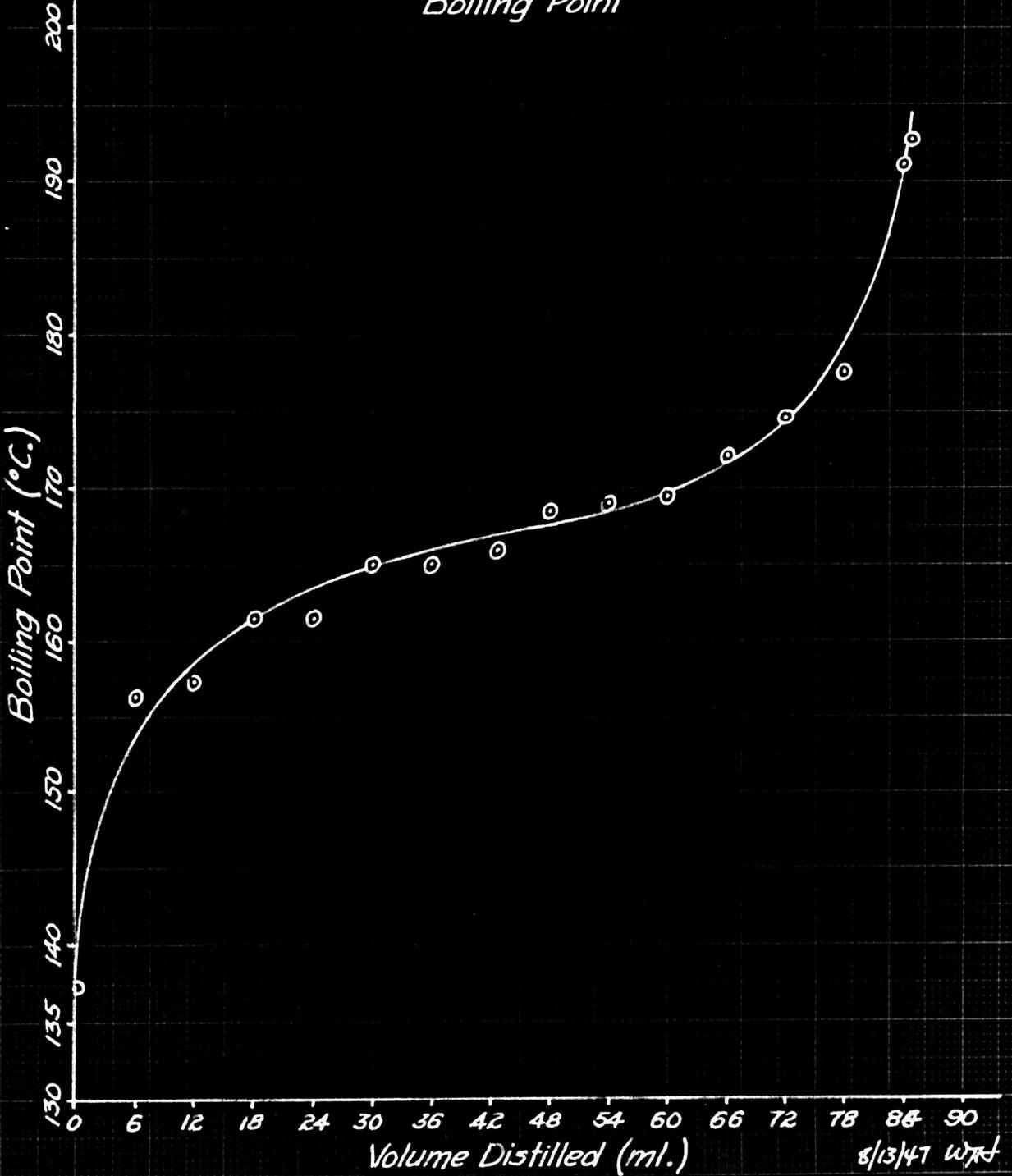
### Graphs 11, 12, and 13

Graph 11, Volume Distilled vs. Boiling Point, on the following page, is the true-boiling-point curve for the middle fraction (155°-182° C.) of Run F.D.-1.

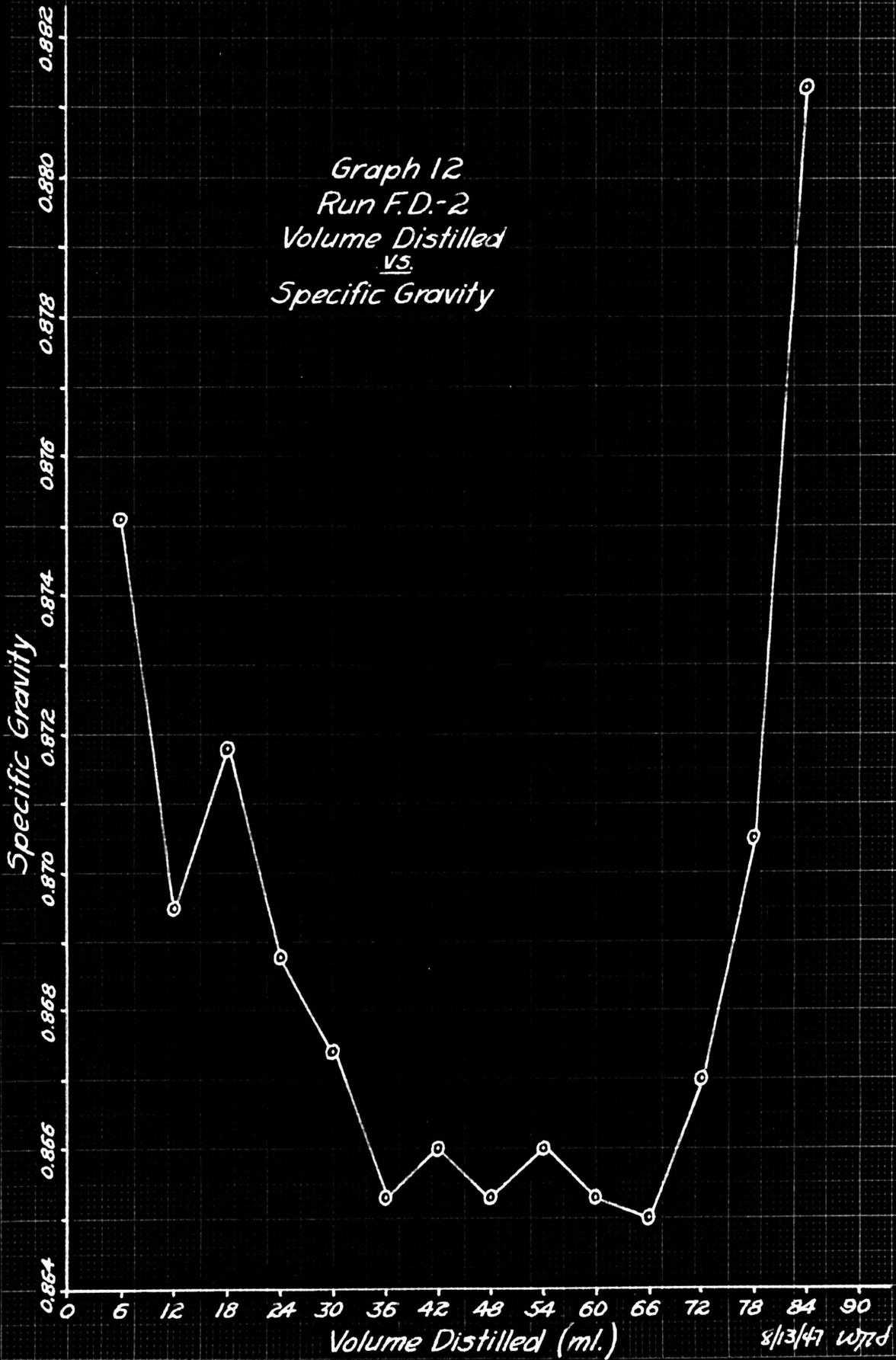
Graph 12, Volume Distilled vs. Specific Gravity, on the second page following, indicates the change in specific gravity due to fractional distillation, or increase in boiling point.

Graph 13, Volume Distilled vs. Refractive Index, on the third page following, indicates refractive index varying with the amount distilled, or the increase in boiling point.

Graph 11  
Run F.D.-2  
Volume Distilled  
vs.  
Boiling Point



Graph 12  
Run F.D.-2  
Volume Distilled  
vs.  
Specific Gravity



Graph 13  
Run F.D.-2  
Volume Distilled  
vs.  
Refractive Index

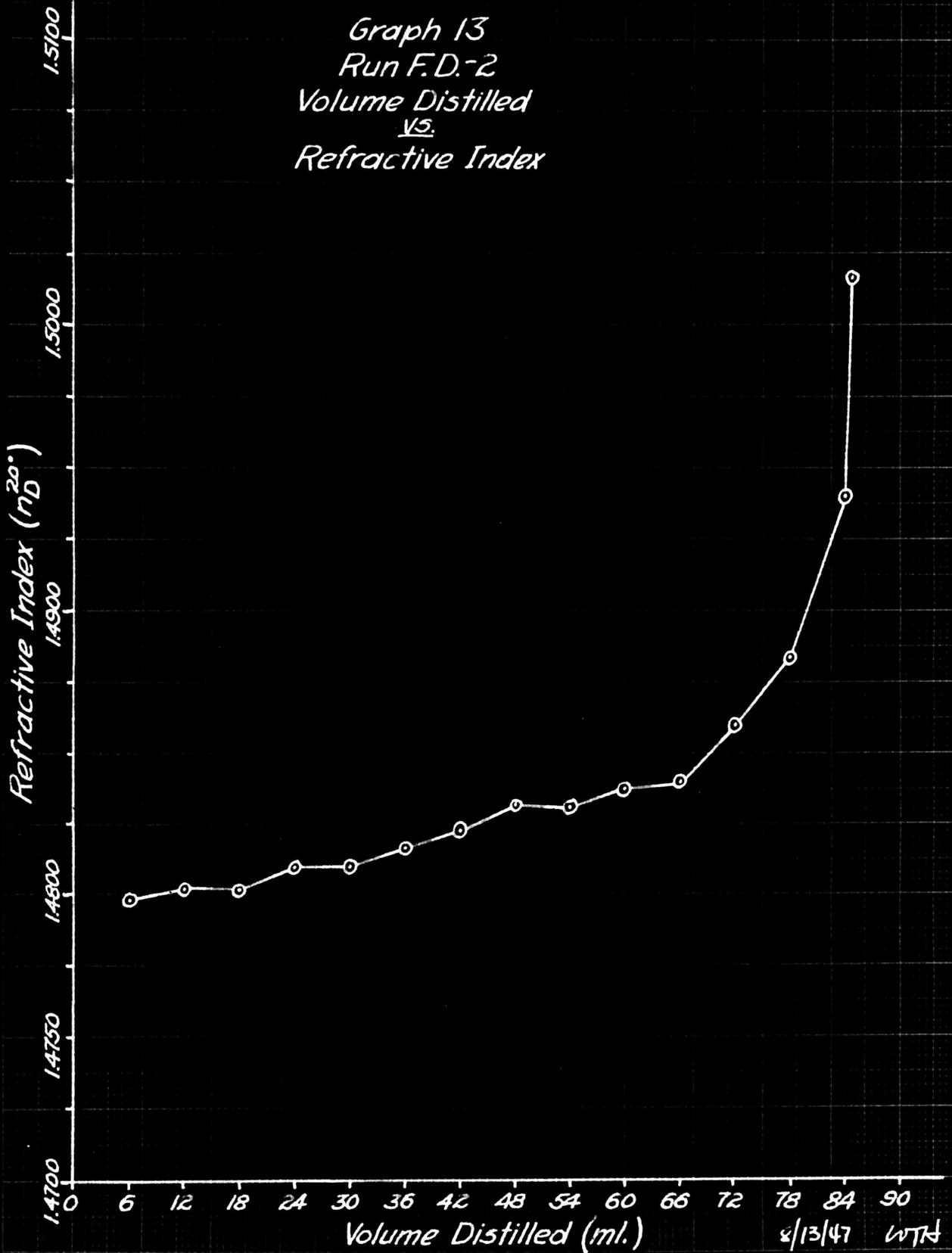


Table VIII

Fractional Distillation of Top Fraction (187°-261° C.)

of Run F.D.-1

Run F.D.-3

Date - May 9, 1947  
 Atmospheric temperature - 23.0° C.  
 Atmospheric pressure - 713.9 mm. Hg, abs.  
 Amount of charge - 46.0 ml.  
 Distillation rate - 2 ml./min.  
 Time of start - 1400  
 Time from start of first vapor - 0 hr., 14 min., 05 sec.  
 Duration of total reflux - 5 min.  
 Flask temperature during total reflux - 163° C.

Bottle No.	Amount Distilled ml.	Temperatures		Sp. Gr.**	n <sub>D</sub> <sup>20°</sup>
		Flask °C.	Vapors* °C.		
-	0	200	157.4	--	--
1	6	207	180.6	0.8910	1.4962
2	12	216	192.1	0.9095	1.5050
3	18	226	202.7	0.9380	1.5158
4	24	234	209.7	0.9641	1.5223
5	30	243	219.8	0.9824	1.5272
6	36	263	230.3	0.9920	1.5329
7	42	329	250.0	0.9986	1.5408
8	42.5	335	253.0	--	1.5368

\* Temperature corrected for thermometer stem and atmosphere.

\*\* Specific gravity corrected for temperature and pycnometer.

Results of Fractional Distillation

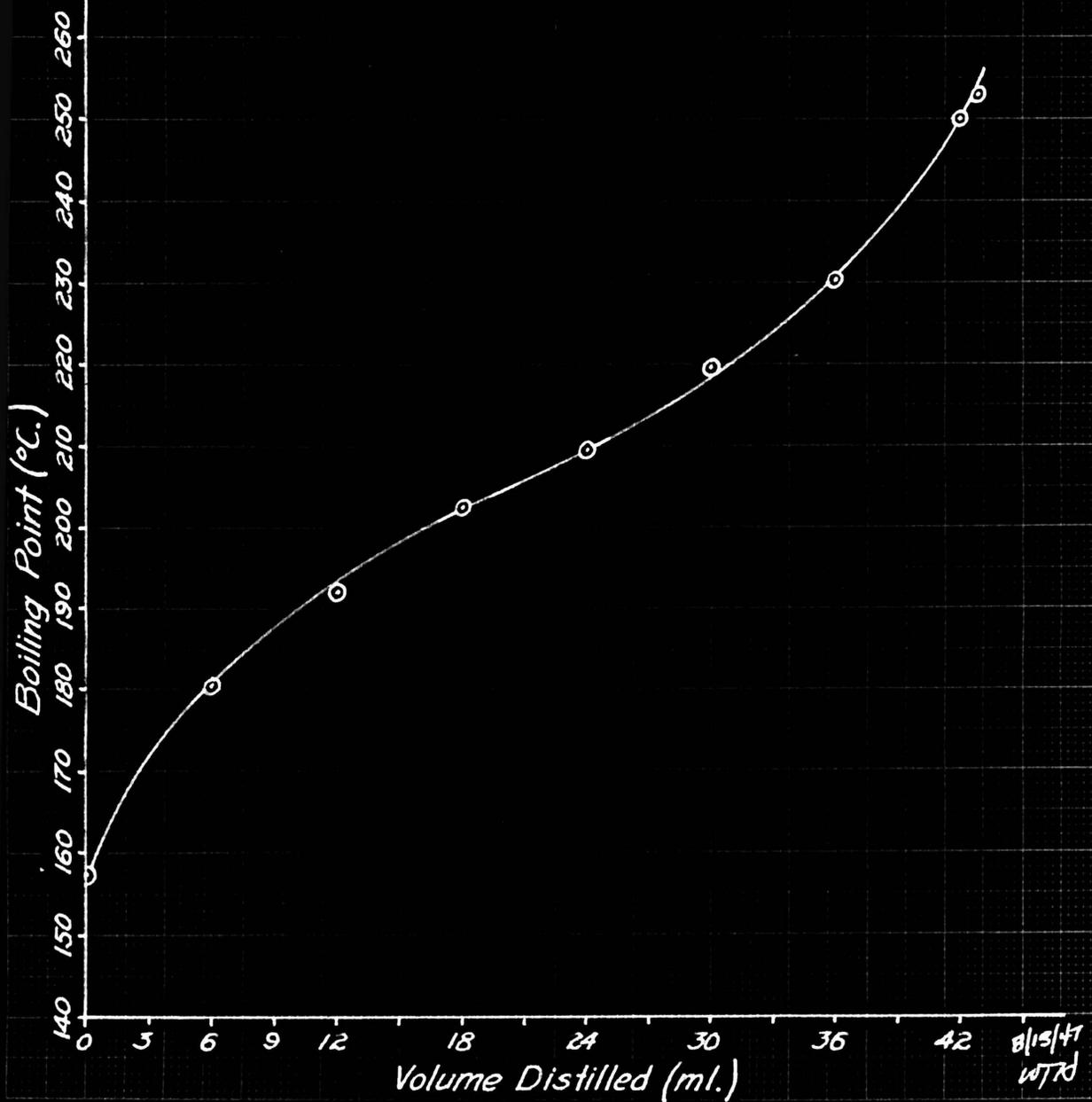
Graphs 14, 15, and 16

Graph 14, Volume Distilled vs. Boiling Point, on the following page, is the true-boiling-point curve for the top fraction (187<sup>o</sup>-261<sup>o</sup> C.) of Run F.D.-1.

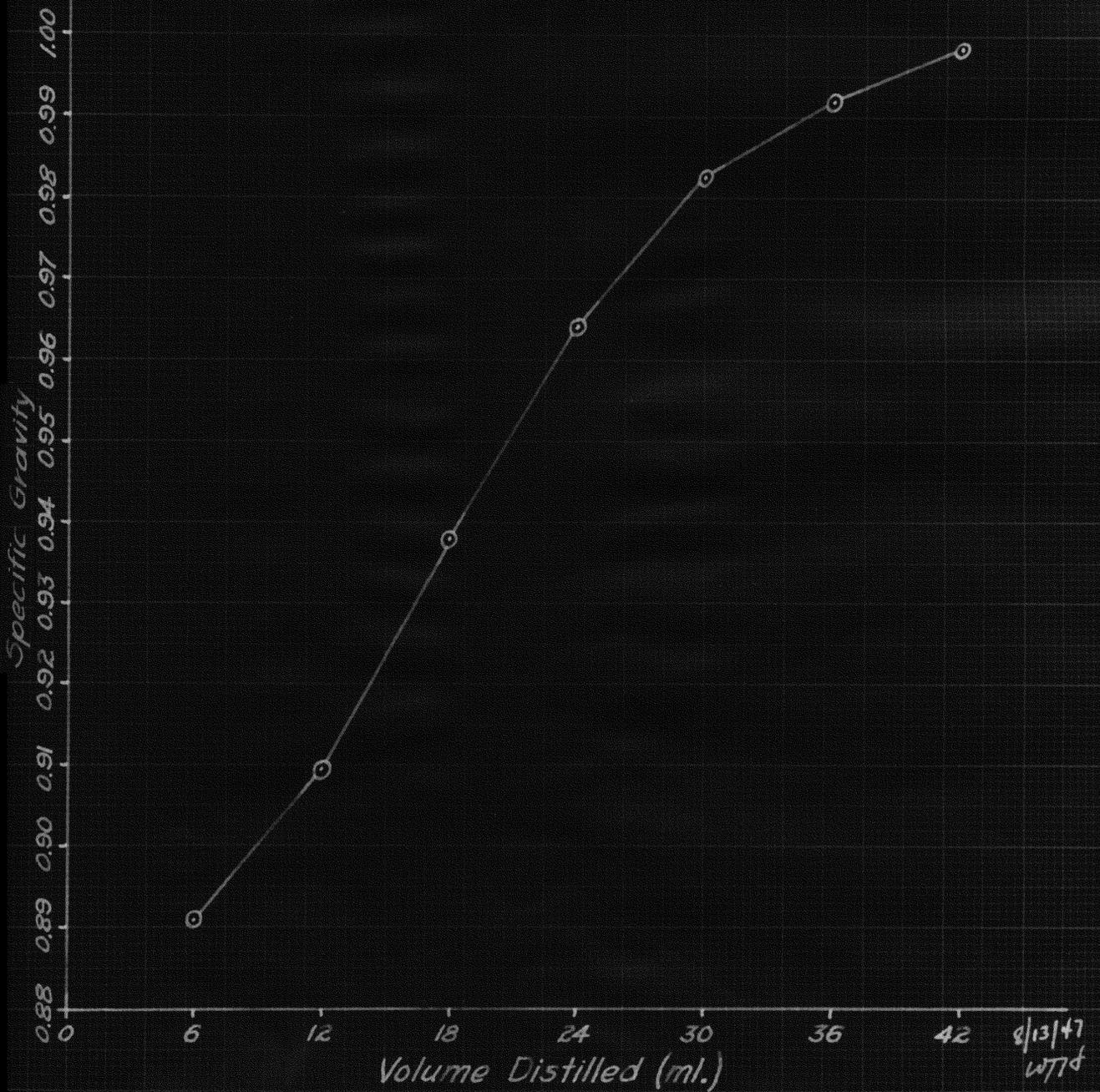
Graph 15, Volume Distilled vs. Specific Gravity, on the second page following, indicates specific gravity varying with the amount distilled, or the increase in boiling point.

Graph 16, Volume Distilled vs. Refractive Index, on the third page following, indicates the change in refractive index with the change in amount distilled, or the increase in boiling point.

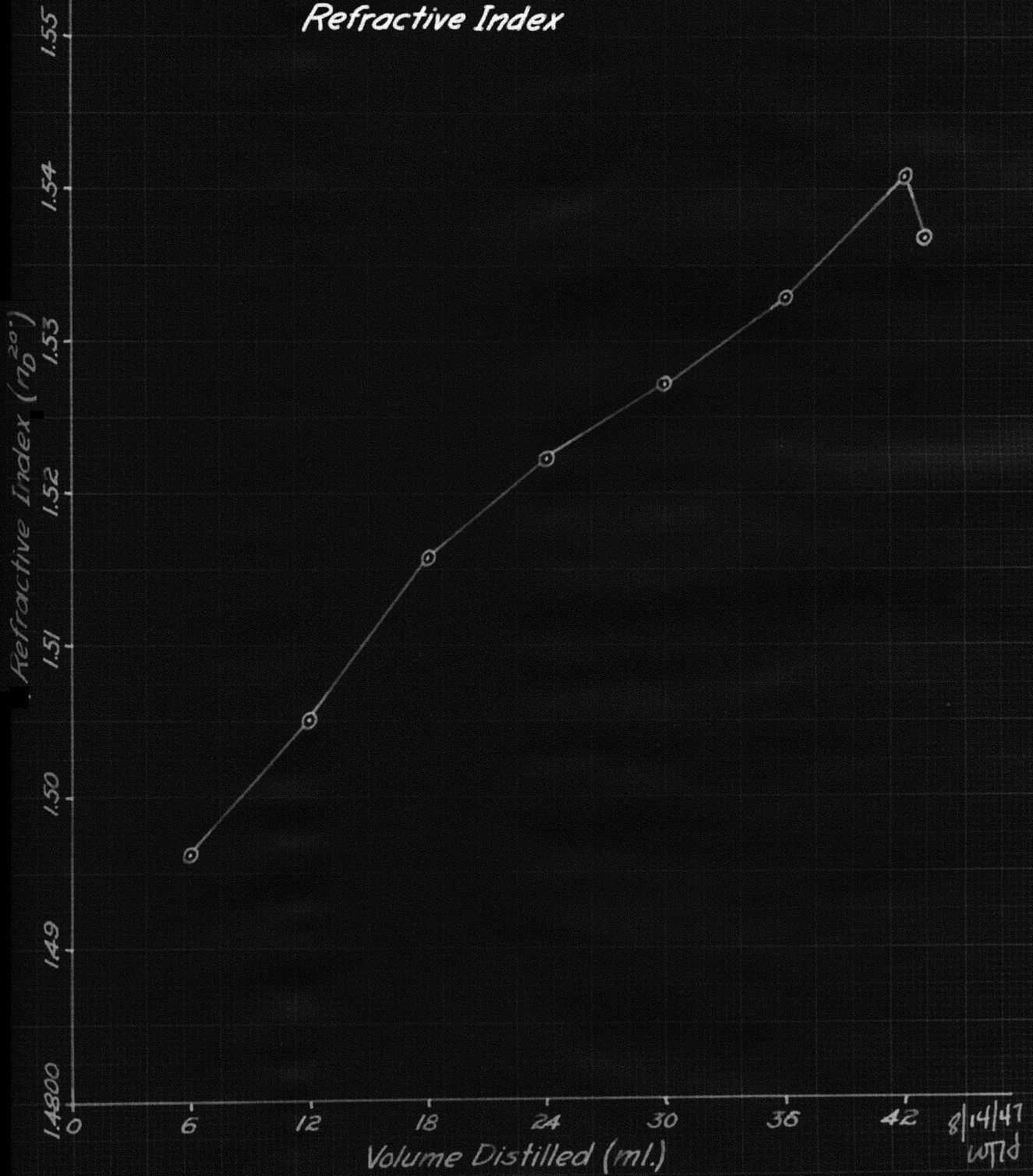
Graph 14  
Run F.D.-3  
Volume Distilled  
vs.  
Boiling Point

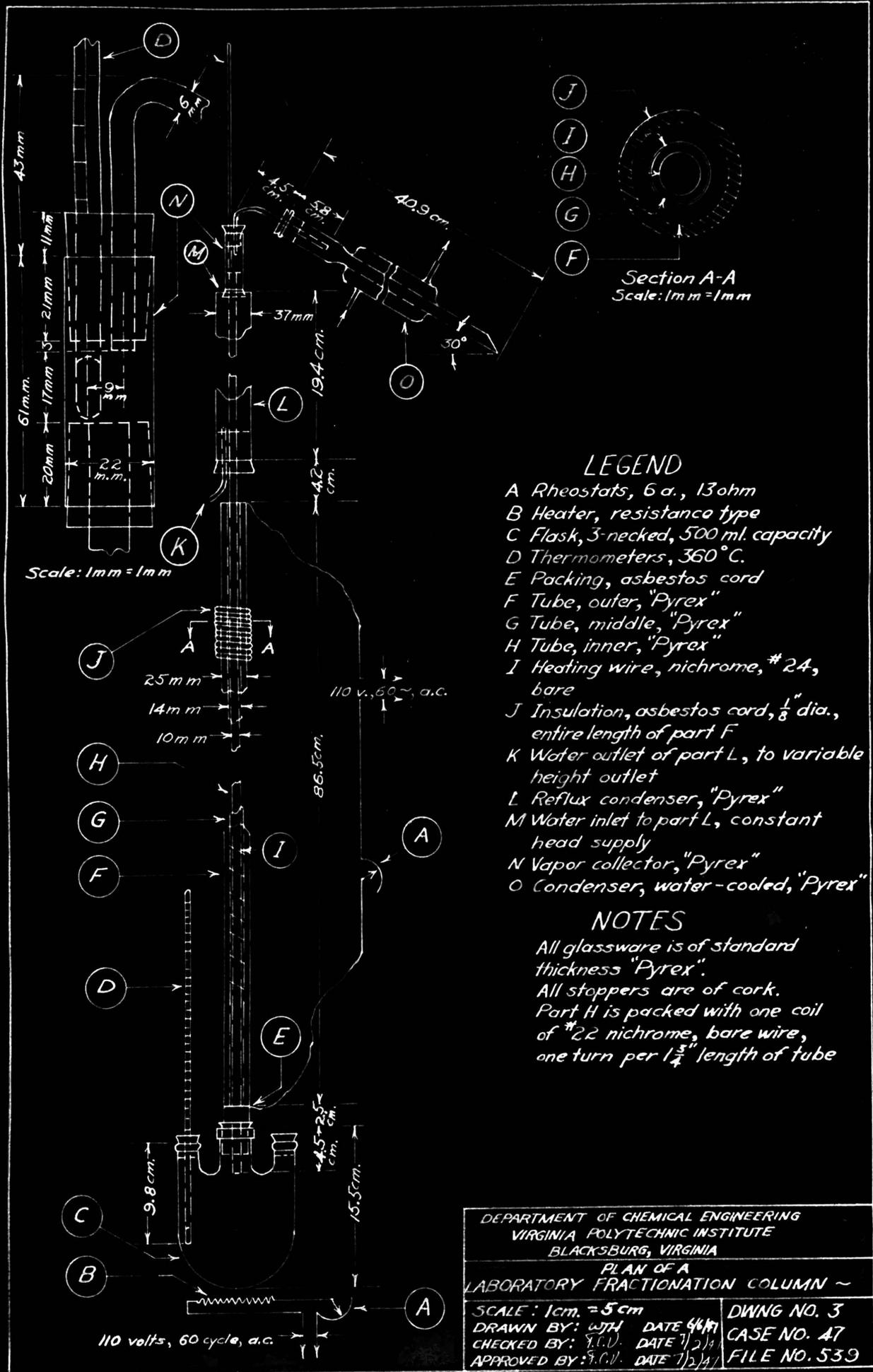


Graph 15  
Run F.D.-3  
Volume Distilled  
vs  
Specific Gravity



Graph 16  
Run F.D.-3  
Volume Distilled  
vs  
Refractive Index





**LEGEND**

- A Rheostats, 6  $\alpha$ , 13ohm
- B Heater, resistance type
- C Flask, 3-necked, 500 ml. capacity
- D Thermometers, 360° C.
- E Packing, asbestos cord
- F Tube, outer, "Pyrex"
- G Tube, middle, "Pyrex"
- H Tube, inner, "Pyrex"
- I Heating wire, nichrome, # 24, bare
- J Insulation, asbestos cord,  $\frac{1}{8}$ " dia., entire length of part F
- K Water outlet of part L, to variable height outlet
- L Reflux condenser, "Pyrex"
- M Water inlet to part L, constant head supply
- N Vapor collector, "Pyrex"
- O Condenser, water-cooled, "Pyrex"

**NOTES**

All glassware is of standard thickness "Pyrex".  
 All stoppers are of cork.  
 Part H is packed with one coil of #22 nichrome, bare wire, one turn per  $1\frac{3}{4}$ " length of tube

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
PLAN OF A LABORATORY FRACTIONATION COLUMN ~	
SCALE: 1cm. = 5cm DRAWN BY: WJH DATE 4/17/47 CHECKED BY: F.C.V. DATE 7/2/47 APPROVED BY: F.C.V. DATE 7/2/47	DWING NO. 3 CASE NO. 47 FILE NO. 539

Table IX

## Chemical Processing

## Formation of Terpeneol from Pinene

Run number	T.P.-1a	T.P.-2a	T.P.-3a	T.P.-4a	T.P.-5a	T.P.-6a
Date, 1947	May 16	May 17	May 19	May 21	May 22	May 24
Materials refluxed:						
Sulfuric acid (98%), ml.	0.75	1.00	5.00	5.00	3.75	3.00
Acetic acid (glacial), ml.	5.00	5.00	25.00	25.00	25.00	15.00
Pinene, ml.	2.30	2.30	11.50	11.50	11.50	11.50
Water (distilled), ml.	27.0	27.0	135	70.0	27.0	27.0
Refr. ind. of pinene, $n_D^{20}$	1.4664	1.4664	1.4664	1.4664	1.4664	1.4664
Atm. press., mm. Hg, abs.	713.2	715.0	710.5	707.9	713.9	715.5
Atm. temp., ° C.	28.0	22.0	24.5	21.0	23.0	25.0
Reflux temp., ° C.	95.0	94.0	98.5	93.5	94.5	99.5
Total time of reflux, hrs.	1	1	1	1	2	2
Refr. ind. of product, $n_D^{20}$	1.4762	1.4690	1.4762	1.4678	1.4748	1.4703
Distillation of product:						
Date, 1947			May 20	May 22	May 23	May 26
Amount charged, ml.			9.75	10.6	10.5	10.2
Atm. press., mm. Hg, abs.			710.2	713.6	714.9	713.0
Atm. temp., ° C.			22.0	23.0	23.0	26.5
Boiling range, ° C.			to 158	to 159	to 180	to 170
Amt. distillate, ml.			7.15	7.10	7.10	7.20
Amt. residue, ml.			0.65	2.00	2.90	2.05
Refr. ind. distillate, $n_D^{20}$			1.4661	1.4671	1.4722	1.4692
Refr. ind. residue, $n_D^{20}$			1.4853	1.4811	1.5005	1.4951
Per cent conversion, calculated			9	10	6	10

Table X

Chemical Processing

Formation of Terpeneol from Pinene

Run number	T.P.-1b	T.P.-2b	T.P.-3b	T.P.-4b	T.P.-5b	T.P.-6b
Date, 1947	May 28	May 29	June 25	June 25	June 26	June 26
Materials charged:						
Ethyl alcohol (95%), ml.	50.0	10.0	30.0	20.0	20.0	20.0
Pinene, ml.	11.5	10.0	10.0	10.0	25.0	20.0
Sulfuric acid (98%), ml.	1.5	3.3	1.9	2.2	4.4	6.6
Water (distilled), ml.	30.0	6.6	8.1	7.2	15.6	23.4
Atm. press., mm. Hg, abs.	712.7	709.6	713.6	714.5	711.6	713.4
Atm. temp., °C.	28.0	27.5	25.5	26.0	27.0	28.0
RPM of stirrer	1000	1000	1000	1000	1000	1000
Mixture temp., °C.						
0 min.	26.0	27.5	27.0	28.0	28.2	29.5
2 min.	24.0	24.5	27.0	28.0	28.5	30.0
4 min.	23.0	24.5	27.0	28.2	28.8	30.0
6 min.	21.5	23.5	27.0	28.2	29.0	30.0
8 min.	20.0	23.5	27.3	28.2	29.0	30.0
10 min.	19.5	23.0	27.3	28.2	29.0	30.2
30 min.	16.0	23.0	28.0	28.3	29.5	30.8
60 min.	16.0	--	28.8	29.2	30.0	31.2
90 min.	--	--	29.0	29.2	30.6	31.6
120 min.	--	--	29.2	29.6	30.5	31.5
180 min.	--	--	29.5	30.0	30.8	31.5
Total time of contact, hrs.	18.5	121	3	3	3	3
Amt. of product, ml.	10.5	9.5	8.7	9.2	24.7	19.2
Refr. ind. of product, $n_D^{20}$	1.4653	1.5220	1.4634	1.4650	1.4647	1.4648
Per cent conversion, calculated	0	0	0	0	0	0

Table XI

Chemical Processing

Formation of Terpin Hydrate from Pinene

Run number	Ter.-1a	Ter.-2a	Ter.-3a
Date, 1947	June 5	June 5	June 5
Materials charged:			
Pinene, ml.	20.0	20.0	20.0
Ethyl alcohol (95%), ml.	5.0	5.0	7.0
Hydrochloric acid (sp. gr. 1.16), ml.	5.0	5.0	5.0
Atm. press., mm. Hg, abs.		714 - 720	
Atm. temp., °C.		25 - 28	
Total time of mixing, min.	1	0	0
Total time of contact, hrs.	42	42	42
Amt. terpin hydrate formed, gms.	0	0	0

Table XII

Chemical Processing

Formation of Terpin Hydrate from Pinene

Run number, Ter.-	1b	2b	3b	4b	5b
Date, 1947	June 5	June 5	June 5	June 5	June 5
Materials charged:					
Pinene, ml.	10	10	10	10	20
Ethyl alcohol (95%), ml.	10	10	10	10	30
Sulfuric acid (25%), ml.	10	10	10	10	20
Atm. press., mm. Hg, abs.			715 - 719		
Atm. temp., °C.			24 - 27		
Total time of heating, hrs.	0	1	1	1	1.5
Temp. of heating, °C.	25	50	75	82	84
Total time of contact, hrs.	24	24	24	24	1
Amt. terpin hydrate formed, gms.	0	0	0	0	0

Table XIII

Chemical Processing

Formation of Terpin Hydrate from Dipentene

Run number	Ter.-1c	Ter.-1d	Ter.-1e
Date, 1947	July 1	July 2	July 3
Materials refluxed:			
Dipentene, ml.	10.0	10.0	10.0
Sulfuric acid (98%), ml.	2.2	--	--
Benzene sulfonic acid, gms.	--	9.98	9.78
Acetic acid (glacial), ml.	--	--	50.0
Water (distilled), ml.	7.8	10.0	--
Atm. press., mm. Hg, abs.	713.0	713.2	714.4
Atm. temp., °C.	29.0	29.0	28.5
Total time of reflux, hrs.	1	2.5	1
Temp. of reflux, °C.	97.5	97.5	110.0
Amt. product, ml.	6.85	7.5	6.0
Refr. ind. product, $n_D^{20}$	1.4744	1.5047	1.5323
Amt. terpin hydrate, gms.	0	0	0

Table XIV

Chemical Processing

Formation of Dipentene from Pinene

Run D-1

Date - June 24, 1947  
Amount of pinene used - 100 ml.  
Refractive index of pinene used - 1.4658  
Atmospheric pressure - 714.8 mm. Hg, abs.  
Atmospheric temperature - 25.5° C.  
Time of start - 1310

Temperature	Pressure	Time from Start	Amount Taken	Ref. Ind.
°C.	psig.	hr.-min.-sec.	ml.	$n_D^{20^\circ}$
150	0	0-33-45	1	1.4658
160	2	0-39-30	2	1.4658
170	5.5	0-46-05	2	1.4658
180	12.1	0-48-30	2	1.4658
190	19.7	0-49-25	2	1.4658
200	30.0	0-52-20	2	1.4658
210**				

\*\* Run stopped due to faulty equipment

Graph 17

Graph 17, Pressure and Refractive Index vs. Temperature on the following page, indicates pressure varying with temperature and no change in refractive index due to increase in temperature.

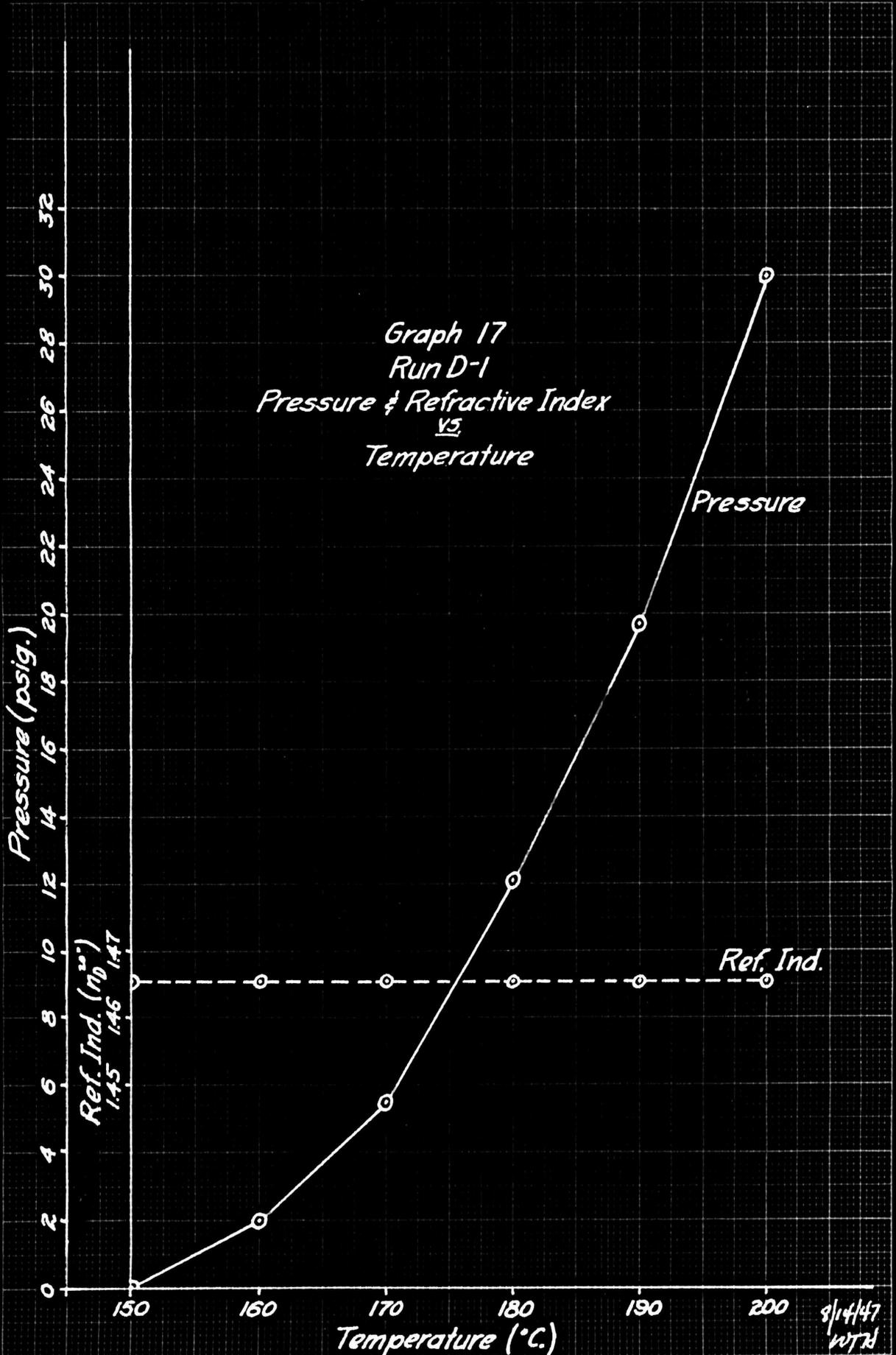


Table XV

Chemical Processing

Formation of Dipentene from Pinene

Run D-2

Date - June 27, 1947  
Amount of pinene used - 100 ml.  
Refractive index of pinene used - 1.4651  
Atmospheric pressure - 712.3 mm. Hg, abs.  
Atmospheric temperature - 28.0° C.  
Time of start - 1420

Temperature	Pressure	Time from Start	Amount Taken	Ref. Ind.
°C.	psig.	hr.-min.-sec.	ml.	$n_D^{20^\circ}$
160	2.0	0-08-30	2	1.4651
170	8.0	0-16-30	2	1.4651
180	14.0	0-23-30	2	1.4651
190	20.5	0-31-15	2	1.4651
200	27.5	0-38-00	2	1.4651
210	36.0	0-47-00	2	1.4651
220	46.5	0-51-15	2	1.4651

230\*\*

\*\* Run stopped due to faulty equipment.

Graph 18

Graph 18, Pressure and Refractive Index vs. Temperature, on the following page, indicates pressure varying with temperature and no change in refractive index due to temperature increase.

Graph 18  
Run D-2  
Pressure & Refractive Index  
vs.  
Temperature

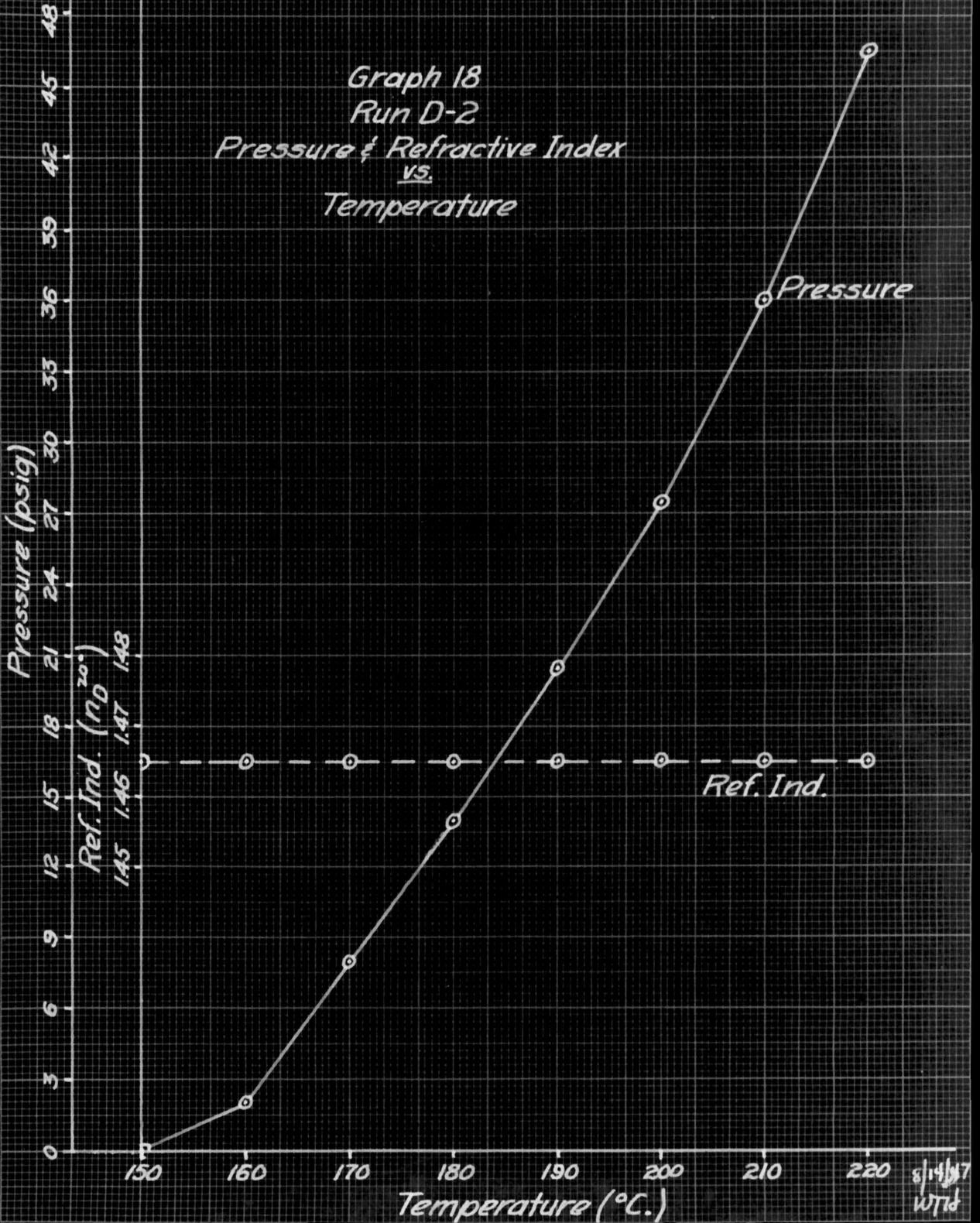


Table XVI

Chemical Processing

Formation of Dipentene from Pinene

Run D-3

Date - June 27, 1947  
Amount of pinene used - 100 ml.  
Refractive index of pinene used - 1.4648  
Atmospheric pressure - 713.8 mm. Hg, abs.  
Atmospheric temperature - 27.0° C.  
Time of start - 1930

Temperature °C.	Pressure psig.	Time from Start hr.-min.-sec.	Refractive Index $n_D^{20}$
200	27.5	0-40-30	1.4648
210	35.5	0-44-35	1.4648
220	46.0	0-48-30	1.4648
230	56.5	0-52-40	1.4652
240	45.5	0-56-00	1.4661
250**			

\*\* Run stopped due to faulty equipment

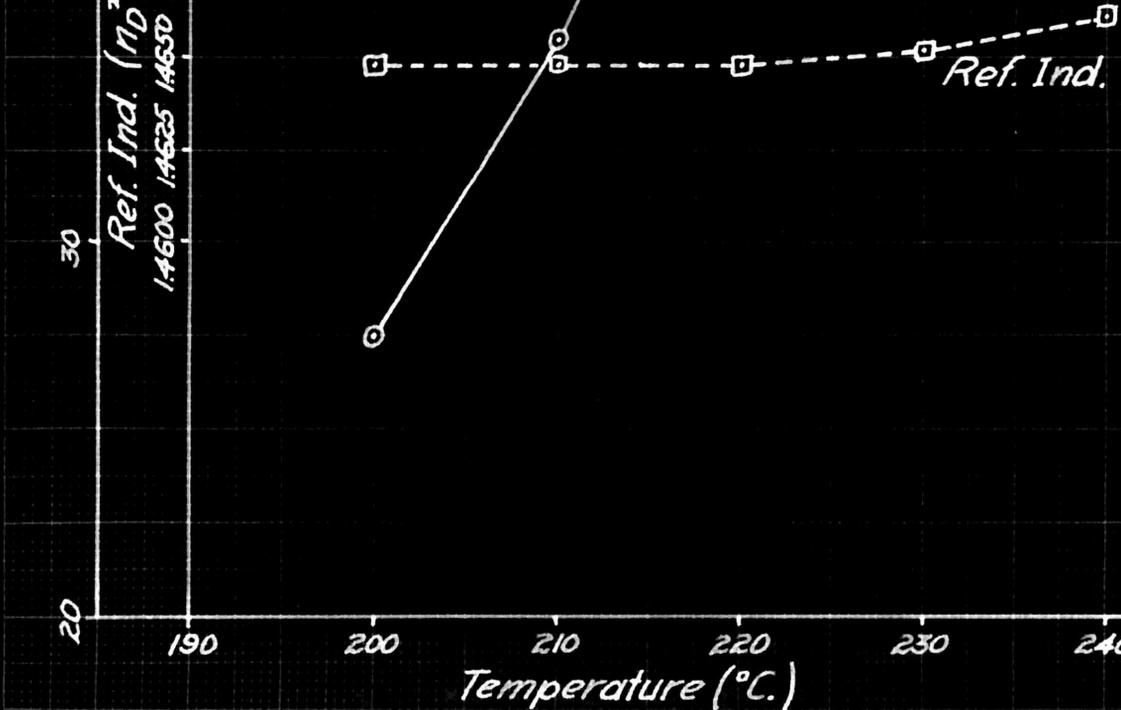
Graph 19

Graph 19, Pressure and Refractive Index vs. Temperature on the following page, indicates the change in pressure as the temperature increases and the variation of refractive index with temperature.

Graph 19  
Run D-3  
Pressure & Refractive Index  
vs.  
Temperature

Pressure (psig.)

Ref. Ind. ( $n_D^{20}$ )  
1.4600 1.4625 1.4650 1.4675 1.4700



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Table XVII

Chemical Processing

Formation of Dipentene from Pinene

Run D-4

Date - June 28, 1947  
Amount of pinene used - 100 ml.  
Refractive index of pinene used - 1.4658  
Atmospheric pressure - 713.1 mm. Hg, abs.  
Atmospheric temperature - 28.5° C.  
Time of start - 1840

Temperature °C.	Pressure psig.	Time from Start hr.-min.-sec.	Refractive Index $n_D^{20^\circ}$
200	27.0	0-44-07	1.4658
210	36.5	0-47-50	1.4654
220	46.5	0-51-45	1.4650
230	57.5	0-56-00	1.4652
240	71.0	1-00-20	1.4658
250	84.5	1-05-20	1.4673
260	95.0	1-10-40	1.4712
270	98.0	1-16-00	1.4785
280	80.0	1-21-00	1.4850
290	65.0	1-26-40	1.4891
300	44.0	1-31-55	1.4881
310	33.0	1-35-55	1.4848
320	10.0	1-39-00	1.4802
330	0.0	1-43-50	1.4747

Chemical Processing

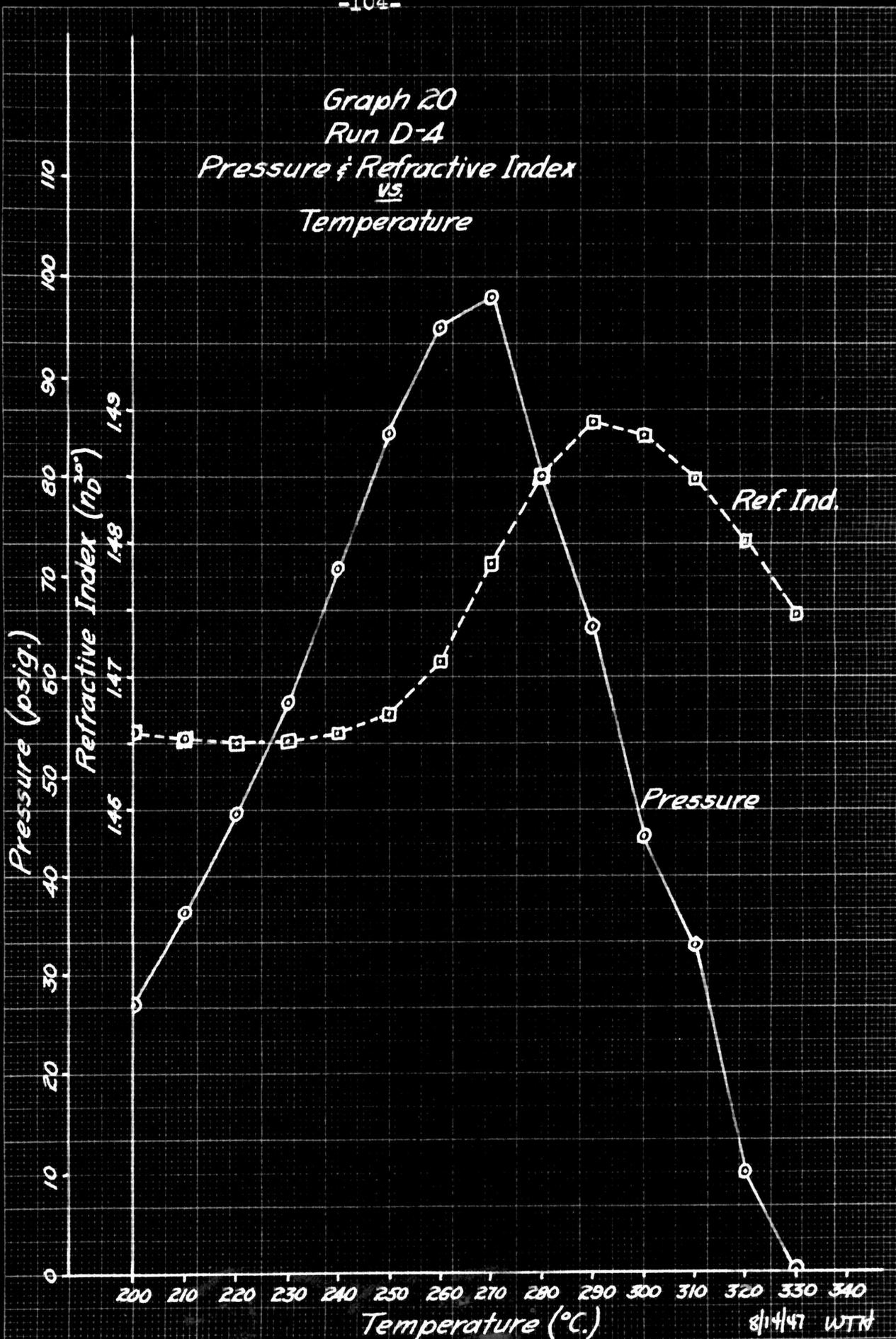
Formation of Dipentene from Pinene

Run D-4

Graph 20

Graph 20, Pressure and Refractive Index vs. Temperature, on the following page, indicates the change of refractive index due to the increase in temperature. The change in pressure first increases with increase in temperature and then decreases, the latter case being due to continued removal of the autoclave contents.

Graph 20  
Run D-4  
Pressure & Refractive Index  
vs.  
Temperature



8/14/47 WTD

Table XVIII

Chemical Processing

Formation of Dipentene from Pinene

Run D-5

Date - June 28, 1947  
Amount of pinene used - 100 ml.  
Refractive index of pinene used - 1.4652  
Atmospheric pressure - 713.1 mm. Hg, abs.  
Atmospheric temperature - 27.0° C.  
Time of start - 2030

Temperature °C.	Pressure psig.	Time from Start hr.-min.-sec.	Refractive Index $n_D^{20^\circ}$
230	63	0-26-00	1.4657
240	77	0-28-10	1.4660
250	93	0-30-30	1.4668
260	106	0-33-15	1.4694
270	103**	0-35-55	1.4742
280	81	0-35-50	1.4799
290	60	0-39-55	1.4864
300	45	0-42-10	1.4908
310	33	0-44-40	1.4888
320	23	0-47-15	1.4843
330	15	0-50-05	1.4793
340	11	0-53-15	1.4744
350	5	0-56-25	1.4740

\*\* Pressure started dropping at 110 psig.

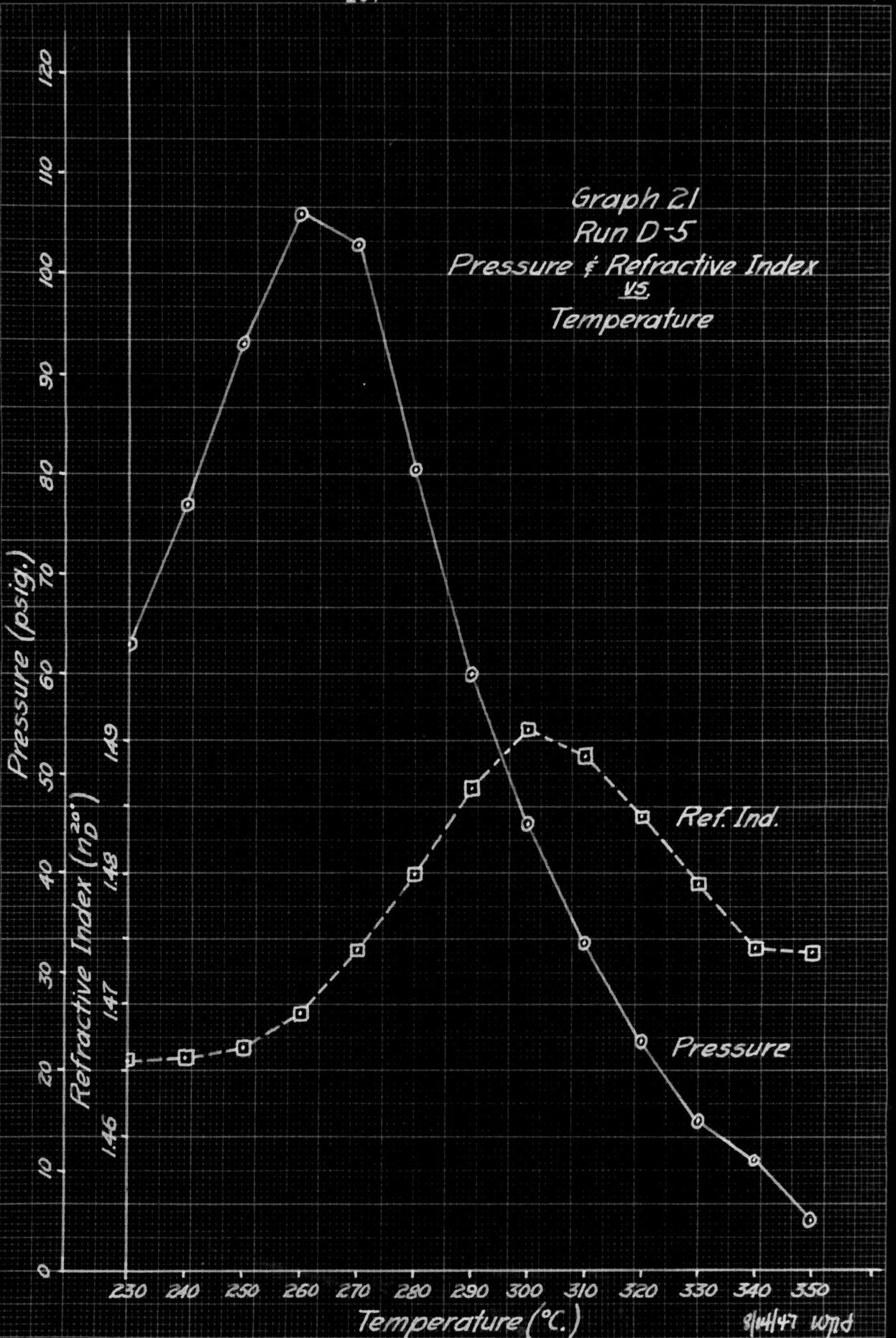
Chemical Processing

Formation of Dipentene from Pinene

Run D-5

Graph 21

Graph 21, Pressure and Refractive Index vs. Temperature, on the following page, indicates the change in pressure and refractive index with increase in temperature. The decrease in pressure in the latter part of the run is due to continued removal of the autoclave contents.



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Table XIX

Chemical Processing

Formation of Dipentene from Pinene

Run D-7

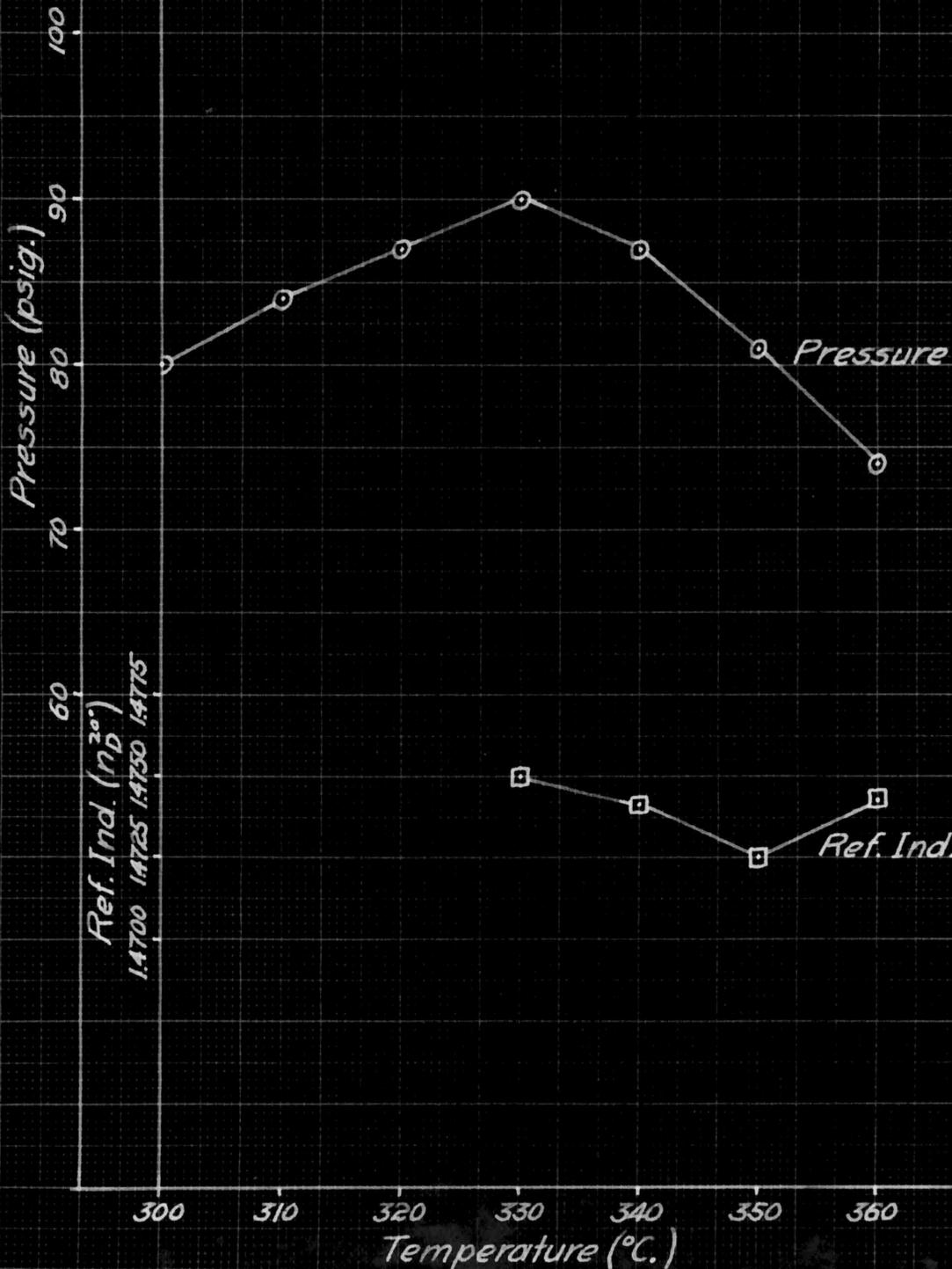
Date - June 30, 1947  
Amount of pinene used - 25 ml.  
Refractive index of pinene used - 1.4652  
Atmospheric pressure - 713.2 mm. Hg, abs.  
Atmospheric temperature - 28.5° C.  
Time of start - 1320

Temperature °C.	Pressure psig.	Time from Start hr.-min.-sec.	Refractive Index $n_D^{20}$
300	80	0-45-00	---
310	84	0-47-35	---
320	87	0-50-30	---
330	90	0-54-25	1.4750
340	87	0-57-15	1.4742
350	81	1-02-40	1.4725
360	74	1-05-45	1.4744

Graph 22

Graph 22, Pressure and Refractive Index vs. Temperature, on the following page, indicates the change in pressure and refractive index as the temperature increases. The decrease in pressure during the latter part of the run is due to continued removal of the autoclave contents.

Graph 22  
Run D-7  
Pressure & Refractive Index  
vs.  
Temperature



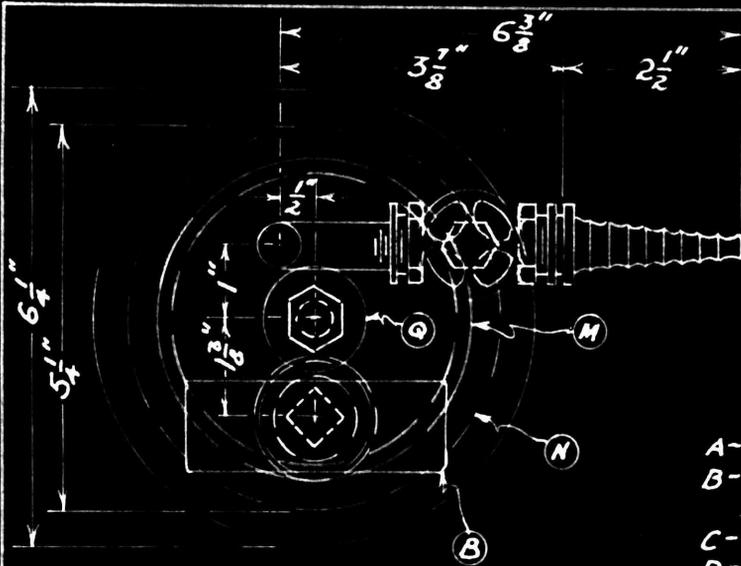
8/14/47  
WTK

Table XX

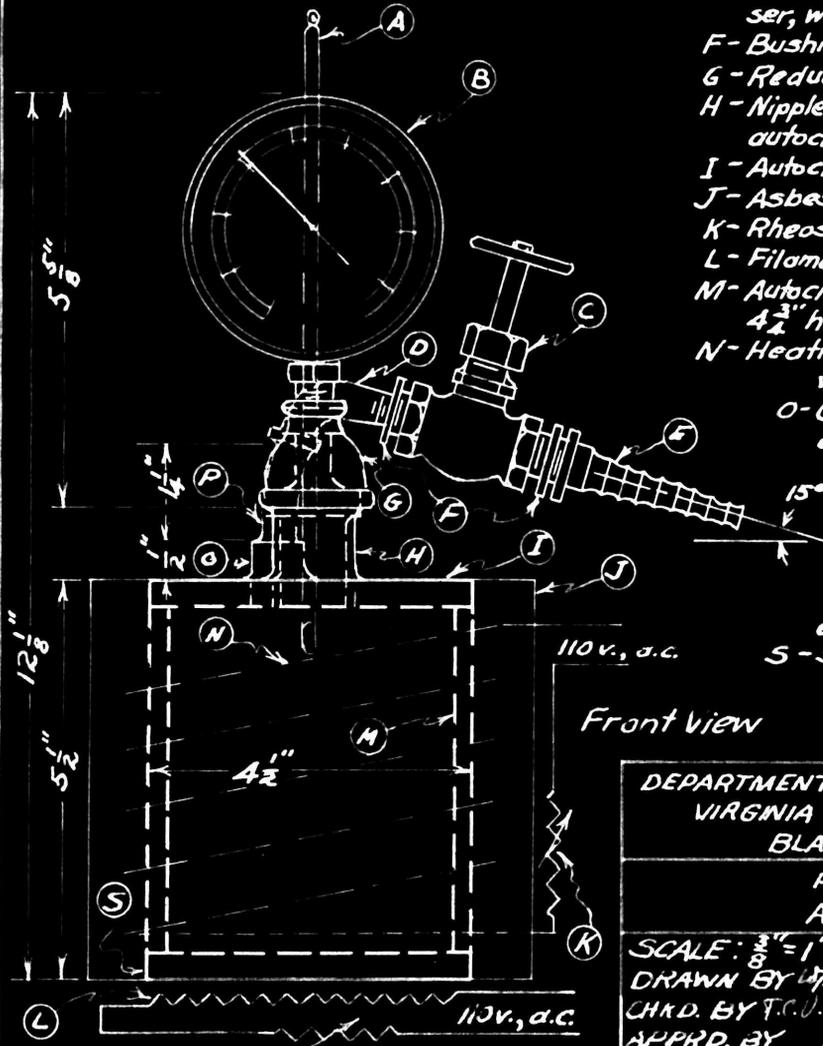
Chemical Processing

Formation of Dipentene from Pinene

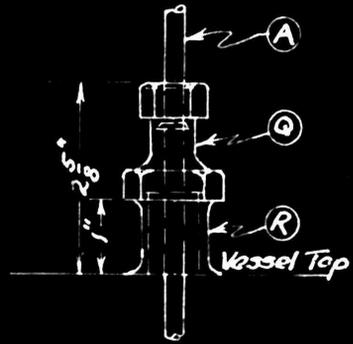
Run number	D-6	D-8	D-9	D-10	D-11	D-12	D-13
Date, 1947	June 29	July 2	July 2	July	July 3	July 4	July 7
Amt. pinene used, ml.	25	35	35	25	25	25	25
Refr. ind. pinene, $n_D^{20}$	1.4652	1.4664	1.4644	1.46	1.4644	1.4644	1.4648
Atm. press., mm. Hg, abs.	714.8	714.0	713.0	714.4	714.0	715.0	711.5
Atm. temp., ° C.	28.0	27.5	30.5	28.5	28.5	28.5	27.5
Total time of heating, hr.-min.-sec.	1-01-30	0-37-00	0-43-10	0-52-30	0-53-20	0-49-10	0-48-00
Final temp., ° C.	360	330	340	360	360	360	360
Final press., psig.	42	45	71	59	107	108	106
Amt. product, ml.	8.7	12.0	17.5	12.5	24.8	23.0	24.0
Refr. ind. product, $n_D^{20}$	1.4740	1.4742	1.4730	1.4740	1.4743	1.4748	1.4748



Plan View



Front View



LEGEND

- A- Thermometer, glass, -10 to 360°C.
- B- Pressure gage, 0 to 150 lb. per sq. in.
- C- Needle valve,  $\frac{3}{8}$ " std., G.I.
- D- Elbow, street,  $\frac{1}{2}$ " std., G.I.
- E- Vapor outlet,  $\frac{1}{4}$ " fitting, to condenser, water-cooled.
- F- Bushings,  $\frac{1}{4}$ " x  $\frac{3}{8}$ ", G.I.
- G- Reducer,  $\frac{1}{4}$ " x  $\frac{3}{8}$ ", std., B.I.
- H- Nipple,  $\frac{3}{4}$ " std., B.I., welded to autoclave top and reducer.
- I- Autoclave top, 15.6" plate, welded.
- J- Asbestos insulation.
- K- Rheostats, 6 amp., 13 ohm.
- L- Filament type heater.
- M- Autoclave body, 4" std. B.I. pipe, 4 1/2" high.
- N- Heating wire, #22 chromel wire, 6' long (c)
- O- Coupling,  $\frac{1}{4}$ " std., G.I., welded to I and P.
- P- Nipple,  $\frac{1}{4}$ " std., G.I., welded to D and O.
- Q- Thermometer stem packing gland.
- R- Nipple,  $\frac{1}{4}$ " std., welded to I and Q.
- S- Same as I.

Note: All welds are  $\frac{3}{8}$ " fillet.

DEPARTMENT OF CHEMICAL ENGINEERING,  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

PLAN OF AN  
AUTOCLAVE

SCALE:  $\frac{3}{8}$ " = 1"  
DRAWN BY *W.P.* DATE 7/17  
CHK'D BY *T.C.O.* DATE 8/26  
APPR'D. BY DATE 8/26

DWNG. NO. 4  
CASE NO. 47  
FILE NO. 539

Table XXI

## Chemical Processing

## Formation of Terpeneol from Dipentene

Run number	T.P.-1d	T.P.-2d	T.P.-3d	T.P.-4d	T.P.-5d
Date, 1947	July 4	July 4	July 6	July 7	July 8
Materials refluxed:					
Dipentene, ml.	10.0	10.0	10.0	10.0	20.0
Sulfuric acid (98%), ml.	3.75	4.5	4.5	4.5	9.0
Acetic acid (glacial), ml.	25.0	25.0	35.0	35.0	50.0
Water (distilled), ml.	27.0	20.0	10.0	15.0	40.0
Atm. press., mm. Hg, abs.	715.0	715.0	714.0	712.0	712.8
Atm. temp., ° C.	28.5	27.5	26.0	27.0	26.0
Total time of reflux, hrs.	2.0	2.0	2.0	2.0	6.0
Reflux temp., ° C.	99.0	106.5	108.5	109.5	108.5
Amt. of product, ml.	8.7	9.2	7.7	8.9	18.8
Refr. ind. of product, $n_D^{20}$	1.4766	1.5012	1.5062	1.4984	1.4943
Distillation of product:					
Amt. of charge, ml.	8.0	8.7	7.4	8.6	18.6
Atm. press., mm. Hg, abs.	715.0	715.0	714.0	712.0	712.8
Atm. temp., ° C.	28.0	27.5	26.0	27.0	26.0
Distillation range, ° C.	to 200				
Amt. of distillate, ml.	7.0	7.4	6.8	6.3	13.7
Amt. of residue, ml.	0.7	0.9	0.4	2.3	4.7
Refr. ind. of distillate, $n_D^{20}$	1.4748	1.4750	1.4732	1.4742	1.4745
Refr. of residue, $n_D^{20}$	1.5139	1.5185	1.5210	1.4828	1.4768
Per cent conversion, calc.	8	8	5	20	26

Sample Calculations for Experimental Data

Density of Non-condensable Vapors

Atmospheric pressure- 715.0 mm. Hg, abs.

Atmospheric temperature- 24.5° C.

Weight of bottle and air- 227.82 gms.

Weight of bottle and vapors- 228.47 gms.

Volume of bottle contents- 352 ml.

Sp. gr. of air at 715 mm. and 24.5° C.- 1.201 gms/l.

1.201 x 0.352 = 0.424 gms. air in bottle

227.82-0.42 = 227.40 gms. wgt. of bottle

228.47-227.40 = 1.07 gms. wgt. of vapors.

$\frac{1.07}{0.352} = 3.05 \times 10^{-3}$  gms/ml. density of vapors

Per Cent Conversion of Dipentene to Terpeneol

Amt. distillate (b.p. below 200°C.)- 13.7 ml.

Amt. residue (b.p. 200-214°C.)- 4.7 ml.

18.4 ml.

4.7/18.4 x 100 = 25.55% approx. terpeneol

assuming incomplete separation:

25% conversion of dipentene to terpeneol

Material Balance

Basis: 100 pounds of terpeneol per 8 hour day  
(all weights in pounds)

Note: left hand- entering; right hand- leaving

A-1 Pine Wood Wastes Storage Yard

Pine Wood Wastes 7,620 Pine Wood Wastes 7,620 → A-2

A-2 Chain Conveyor

A-1 → Same as A-1 Same as A-1 → A-3

A-3 Shredder

A-2 → Same as A-1 Same as A-1 → A-4

A-4 Chain Conveyor

A-3 → Same as A-1 Same as A-1 → B-1

B-1 Retort

A-4 → Pine Wood Wastes 7,620	Charcoal	2,770 → Stor.
	Creosote	167 → Stor.
	Vapors	<u>4,683</u> → B-2
		7,620

B-2 Retort Condenser

B-1 → Vapors	4,683	Condensate	1,460 → B-3
		Non-condensable vapors	<u>3,223</u> → B-3
			4,683

B-3 Vapor Separator

B-2 → Condensate	1,460	Condensate	1,460 → B-4
B-2 → Non-condensable Vapors	<u>3,223</u>	Non-condensable Vapors	<u>3,223</u> → B-1
	4,683		4,683

B-4 Settling Tank No. 1

B-3 → Condensate	1,460	Light Crudes	350.5 → B-8
		Pyroligneous Liquor	147.3 → B-5
		Heavy Crudes	<u>962.2</u> → B-6
			1,460.0

B-5 Waste Acid Pump

B-4 → Pyroligneous Liquor	147.3	Pyroligneous Liquor	147.3 → Waste
------------------------------	-------	------------------------	---------------

B-6 Heavy Crudes Pump

B-4 → Heavy Crudes	962.2	Heavy Crudes	962.2 → B-7
--------------------	-------	--------------	-------------

B-7 Heavy Crudes Storage Tank

B-6 → Same as B-6		Same as B-6	
-------------------	--	-------------	--

B-8 Light Crudes Pump

B-4 → Light Crudes	350.5	Light Crudes	350.5 → B-9
--------------------	-------	--------------	-------------

B-9 Light Crudes Storage Tank

B-8 → Same as B-8		Same as B-8	→ C-1
-------------------	--	-------------	-------

C-1 Light Crudes Fractionator Feed Pump \*\*

B-9 → Same as B-8		Same as B-8	→ C-2
-------------------	--	-------------	-------

C-2 Light Crudes Fractionator \*\*

C-1 → Light Crudes	350.5	Laksol	54.1	→ C-6
C-3 → Steam (200 lb. press.)	11.28	Turpentine	94.4	→ C-3
SP → Steam (200 lb. press.)	<u>11.28</u>	Pine Oil	55.0	→ C-3
		Creosote	147.0	→ Stor.
		Steam	<u>22.56</u>	→ Waste
	373.06		373.06	

C-3 Light Crudes Fractionator Stripping Column \*\*

C-2 → Turpentine	94.4	Turpentine	94.4	→ D-1
C-2 → Pine Oil	55.0	Pine Oil	55.0	→ F-1
SP → Steam (200 lb. press.)	<u>11.28</u>	Steam (200 lb. press.)	<u>11.28</u>	→ C-2
	160.68		160.68	

C-4 Light Crudes Fractionator Reflux Pump \*\*

C-2 → Laksol	216.4	Laksol	216.4	→ C-5
--------------	-------	--------	-------	-------

C-5 Light Crudes Fractionator Reflux Heat Exchanger \*\*

C-4 → Same as C-4		Same as C-4		→ C-2
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C-6 Laksol Condenser No. 1 \*\*

C-2 → Laksol	54.1	Laksol	54.1	→ C-7
--------------	------	--------	------	-------

C-7 Laksol Storage Tank

C-6 → Laksol	54.1	Laksol	60.9	→ C-8
D-6 → Laksol	<u>6.8</u>			
	60.9			

C-8 Laksol Pump

C-7 → Laksol	60.9	Laksol	60.9	
--------------	------	--------	------	--

D-1 Turpentine Pump \*\*

C-3 → Turpentine            94.4            Turpentine            94.4 → D-2

D-2 Turpentine Fractionator \*\*

D-1 → Turpentine	94.4	Laksol	6.8 → D-6
D-3 → Steam (200 lb. press.)	5.67	Pinene	60.6 → D-3
SP → Steam (200 lb. press.)	5.67	Dipentene	27.0 → D-3
		Steam	<u>11.34</u> → Waste
	<u>105.74</u>		105.74

D-3 Turpentine Fractionator Stripping Column \*\*

D-2 → Pinene	60.6	Pinene	60.6 → D-7
D-2 → Dipentene	27.0	Dipentene	27.0 → D-10
SP → Steam (200 lb. press.)	5.67	Steam (200 lb. press.)	<u>5.67</u> → D-2
	<u>93.27</u>		93.27

D-4 Turpentine Fractionator Reflux Pump \*\*

D-2 → Laksol            27.2            Laksol            27.2 → D-5

D-5 Turpentine Fractionator Reflux Heat Exchanger \*\*

D-4 → Same as D-4                            Same as D-4                            → D-2

D-6 Laksol Condenser No. 2 \*\*

D-2 → Laksol            6.8            Laksol            6.8 → C-7

D-7 Pinene Condenser \*\*

D-3 → Pinene            60.6            Pinene            60.6 → D-8

D-8 Pinene Storage Tank

D-7 → Same as D-7                            Same as D-7                            → D-9



F-2 Pine Oil Fractionator \*\*

F-1 → Pine Oil	55.0	Dipentene	20.4 → F-3
		Pine Oil	<u>34.6</u> → F-4
			55.0

F-3 Dipentene Condenser No. 2 \*\*

F-2 → Dipentene	20.4	Dipentene	20.4 → D-11
-----------------	------	-----------	-------------

F-4 Pine Oil Condenser \*\*

F-2 → Pine Oil	34.6	Pine Oil	34.6 → F-7
----------------	------	----------	------------

F-5 Pine Oil Fractionator Reflux Condenser \*\*

F-2 → Dipentene	81.6	Dipentene	81.6 → F-6
-----------------	------	-----------	------------

F-6 Pine Oil Fractionator Reflux Pump \*\*

F-5 → Same as F-5		Same as F-5	→ F-2
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F-7 Pine Oil Pump No. 2 \*\*

F-4 → Same as F-4		Same as F-4	→ F-8
-------------------	--	-------------	-------

F-8 Pine Oil Storage Tank

F-7 → Same as F-4		Same as F-4	
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G-1 Reactor

D-12 → Dipentene	359	Terpineol	100	} → G-2	
D-12 → Pinene	19	Dipentene	256		
H-2 → {	Sulfuric Acid	324	Pinene		14
	Acetic Acid	1,025	Sulfuric Acid		324
	Water	771	Acetic Acid		1,025
MU →	Water	12	Water		771
		<u>2,510</u>	Polymers		<u>20</u>
			<u>2,510</u>		



I-3 Reactor Product Pump No. 2 \*\*

I-2 → Same as I-1                      Same as I-1                      → I-4

I-4 Terpeneol Fractionator Feed Heaters \*\*

Dipentene Section  
Outside tubing

I-5 → Dipentene	256	Dipentene	256 → D-11
I-5 → Pinene	<u>14</u>	Pinene	<u>14</u> → D-11
	270		270

Dipentene Section  
Inside tubing

I-3 → Same as I-1                      Same as I-1                      → TS

Terpeneol Section  
Outside tubing

I-6 → Terpeneol                      100                      Terpeneol                      100 → I-9

Terpeneol Section  
Inside tubing

DS → Same as I-1                      Same as I-1                      → I-5

I-5 Terpeneol Fractionator \*\*

I-4 → {	Terpeneol	100	Terpeneol	100 → I-6
	Dipentene	256	Dipentene	256 → I-4
	Pinene	14	Pinene	14 → I-4
	Polymers	20	Polymers	20 → Waste
I-6 → Steam (200 lb. press.)	24.3	Steam	<u>48.6</u> → Waste	
SP → Steam (200 lb. press.)	<u>24.3</u>		438.6	
	438.6			

I-6 Terpeneol Fractionator Stripping Column \*\*

I-5→Terpineol	100	Terpineol	100→I-4
SP→Steam (200 lb. press.)	<u>24.3</u>	Steam (200 lb. press.)	<u>24.3</u> →I-5
	124.3		124.3

I-7 Terpeneol Fractionator Reflux Condenser \*\*

I-5→Dipentene	256	Dipentene	256→I-8
I-5→Pinene	<u>14</u>	Pinene	<u>14</u> →I-8
	270		270

I-8 Terpeneol Fractionator Reflux Condenser \*\*

I-7→Same as I-7                      Same as I-7                      →I-5

I-9 Terpeneol Pump \*\*

I-4→Terpineol                      100                      Terpeneol                      100 →I-10

I-10 Terpeneol Storage Tank

I-9→Same as I-9                      Same as I-9

Abbreviations and Symbols

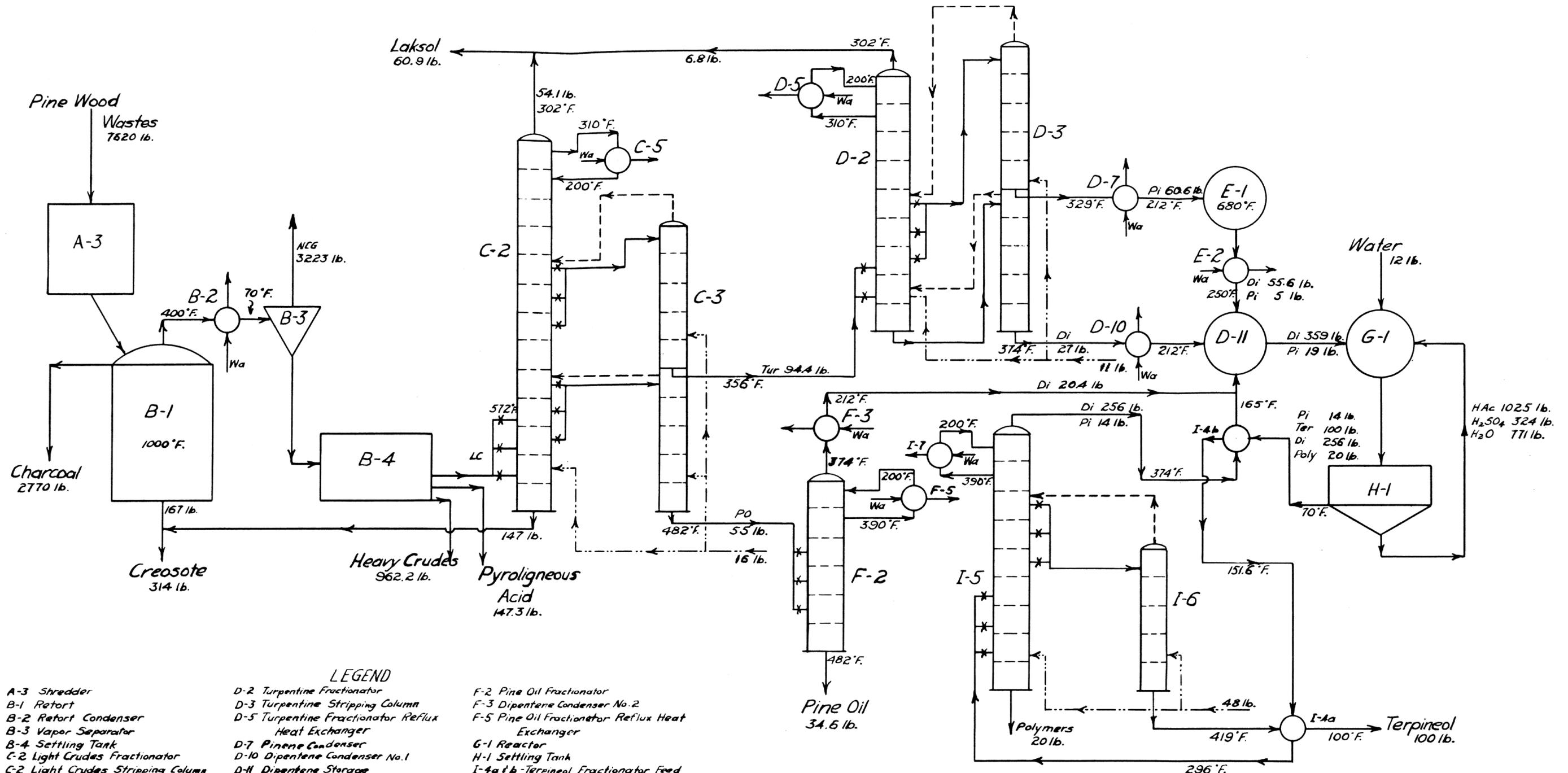
\*\* All equipment thus marked will be run one day for each six days the other equipment is run. The weights shown represent a daily basis.

SP Indicates steam received from the steam plant.

MU Indicates make-up water added in the reactor (G-1).

TS Indicates source as being the Terpeneol side of the Feed Heaters.

DS Indicates the source as being the Dipentene Side of the Feed Heaters.



**LEGEND**

A-3 Shredder  
 B-1 Retort  
 B-2 Retort Condenser  
 B-3 Vapor Separator  
 B-4 Settling Tank  
 C-2 Light Crudes Fractionator  
 C-2 Light Crudes Stripping Column  
 C-5 Light Crudes Fractionator Reflux Heat Exchanger

D-2 Turpentine Fractionator  
 D-3 Turpentine Stripping Column  
 D-5 Turpentine Fractionator Reflux Heat Exchanger  
 D-7 Pinene Condenser  
 D-10 Dipentene Condenser No.1  
 D-11 Dipentene Storage

E-1 Autoclave  
 E-2 Autoclave Product Condenser

F-2 Pine Oil Fractionator  
 F-3 Dipentene Condenser No.2  
 F-5 Pine Oil Fractionator Reflux Heat Exchanger

G-1 Reactor  
 H-1 Settling Tank  
 I-4a & b Terpineol Fractionator Feed Heaters  
 I-5 Terpineol Fractionator  
 I-6 Terpineol Stripping Column  
 I-7 Terpineol Fractionator Reflux Heat Exchanger

**SYMBOLS**

LC - Light Crudes  
 Tur - Turpentine  
 PO - Pine Oil  
 Pi - Pinene

Di - Dipentene  
 Ter - Terpineol  
 Poly - Polymers  
 HAc - Glac. Acetic Acid

H<sub>2</sub>SO<sub>4</sub> - 98% Sulfuric Acid  
 H<sub>2</sub>O - Processed Water  
 Wa - Cooling Water  
 NCG - Non-Condensable Vapors

--- Lower Boiling Portion + Steam  
 - - - - - Stripping Steam at 200 lb. gage

**NOTES**  
 All weights are given on a per day basis.  
 Weights of cooling water are given in Selection of Equipment section.

VIRGINIA POLYTECHNIC INSTITUTE  
 DEPARTMENT OF CHEMICAL ENGINEERING  
 BLACKSBURG, VIRGINIA

Quantitative Flow Sheet  
 for the  
 Production of Terpineol from Destructively Distilled Pine Wood Wastes

SCALE: None	DATE 7/24/47	Drawing No. 5
DRAWN BY	DATE 8/11/47	File No. 47
CHECKED BY	DATE 8/11/47	Case No. 539
APPROVED BY		

## Equipment Specifications

### A-1 Pine Wood Wastes Storage Yard

For size and location in the plant, refer to Drawing No. 7, page 152.

### A-2 Chain Conveyor

Length from center to center: 20 ft. horizontal and 30 ft. on 20° incline.

Capacity: 953 lbs. pine wood per hour, density of 40 lb. per cu. ft. at a speed of 50 ft. per min.

Chain: 1.361 in. pitch, malleable iron, 7.2 lbs. per ft., approx. 74 links per 10 ft., corresponds to Link-Belt chain no. 55.

Attachments: 1½ in. pitch, 4 in. high, malleable iron, 14.5 lbs. per ft., corresponds to Link-Belt attachment no. Y-3.

Power required: for horizontal length- 2 HP motor, 3 phase, 220/440 volts 60 cycle, a.c., splash-proof, induction, 1750 rpm reduced to approx. 31 rpm with speed reducer. For inclined length: 5 HP motor, 220/440 volts, 3 phase, 60 cycle, a.c., splash-proof, induction, 1750 rpm reduced to approx. 31 rpm with speed reducer.

Equipment available from:

Motors- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.

Chain, attachments, and speed reducers- Link-Belt, Chicago, Ill.

Number required:

Motors- one each, 2 HP and 5 HP

Chain- 150 ft.

Attachments- 50 ft.

Speed reducers- 2

The conveyor is placed in the bottom of a trough, the cross section of which is a trapezoid having a bottom base of 2 ft., a top base of 5 ft., and an altitude of 4 ft. The trough is constructed of ½ in. steel plate, spot welded. The top of the trough for the horizontal section is flush with the top of the ground.

### A-3 Shredder

Rotary cutter, overall dimensions 90 in. x 29 in. x 84 in.

Number of knives: 5 fly and 6 bed.

Hopper opening: 60 in x 60 in.

Grinding chamber: 54½ in. long, 18½ in. dia.

Operating speed: 900 rpm or slower

Drive: belt type

Power required: 50 HP motor, 220/440 volts, 3 phase, 50 cycle, squirrel-cage, induction, splash-proof, 900 rpm.

Equipment available from:

Motor- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.

Shredder- Abbe' Engineering Co., New York.

Number required:

Motors- one 50 HP

Shredders- one

### A-4 Chain Conveyor

Length from center to center: 30 ft. on 20° incline.

Capacity: 953 lbs. of pine wood chips, density of approx. 30 lbs., per cu. ft. at a speed of 50 ft. per min.

Chain: 1.506 in. pitch, malleable iron, 8 lbs. per ft., approx. 80 links per 10 ft., corresponds to Link-Belt chain no. 52.

Attachments: 1 1/8 in. long, 2 1/8 in. high, malleable iron, 0.6 lb. per ft., corresponds to Link-Belt scraper no. 57.

Power required: 2 HP motor, 220/440 volts, 3 phase, 60 cycle, a.c., squirrel-cage, induction, splash-proof, 1750 rpm reduced to approx. 33 rpm with speed reducer.

Equipment available from:

Motor- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.

Chain, attachments, and speed reducers- Link-Belt, Chicago, Ill.

Number required:

Motors- one 2 HP

Chain- 75 ft.

Attachments- 50 ft.

Speed reducers- one

The conveyor is placed in the bottom of a trough, the cross section of which is a trapezoid having a bottom base of 1 ft., a top base of 3 ft., and an altitude of 2 ft. The trough is made of ¼ in. steel plate, spot welded.

### B-1 Retort

The drawing and specifications for the retort may be found in Drawing No. 5, page 128.

The specifications for the pine wood chips basket hoist are as follows:

Type: electrically propelled, motor-driven monorails, floor-operated

Capacity: 5 ton

Lift: 18 ft., std.

Lifting speed: 10-15 ft. per min.

Power required: 5 HP, 220/440 volts, 3 phase, 60 cycle, a.c., motor furnished with hoist.

Equipment available from:

Hoist and motor- Euclid Crane and Hoist Co., Harrison N. J.

### B-2 Retort Condenser

Effective length of tubing: 148 ft.

Size of tubing:  $1\frac{1}{2}$  in. O.D., 14 B.w.g. thick

Tube spacing:  $\frac{3}{8}$  in.

Tubing material: bronze

Condenser shell material: cast iron

Baffle type: orifice

Baffle spacing: 12 in.

Condenser type: multi-pass, floating head, counter-current flow

Vapor path: inside tubing enters at 400°F., leaves at 70°F.

Cooling medium: water, enters at 60°F., leaves at 150°F., 1.35 cu. ft. per min. (5040 lbs. per min.)

B-3 Vapor Separator

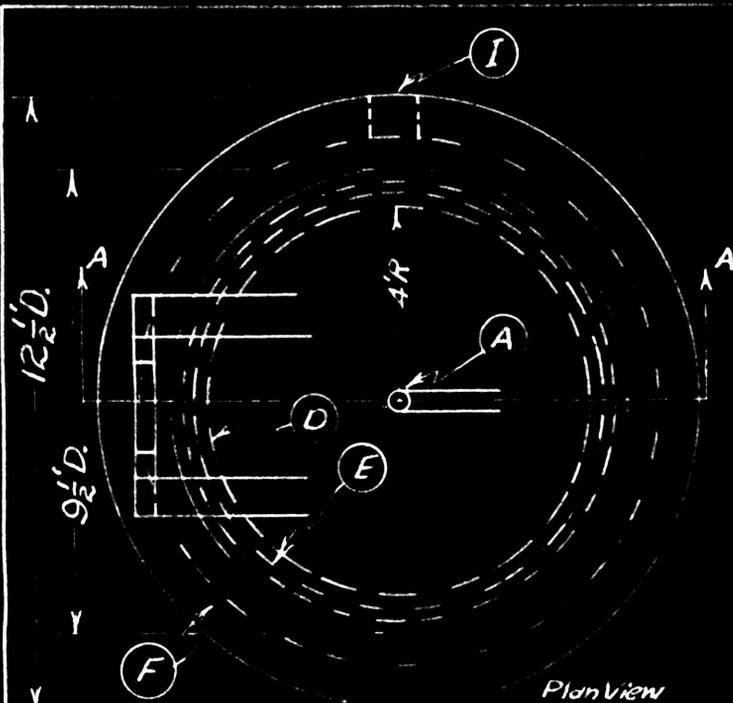
Shape: inverted cone  
Size: 3 ft. high, 2 ft. dia.  
Connections: Condensate enters 2 ft. from bottom tip, non-condensable vapors leave through the top, condensate leaves through the bottom tip.  
Accessories: A float-controlled exit valve maintains a  $2\frac{1}{2}$  ft. head in the separator.  
Material of construction: wood, copper, or concrete.  
Supports: separator is supported at exit end of re-tort condenser.

B-4 Settling Tank No. 1

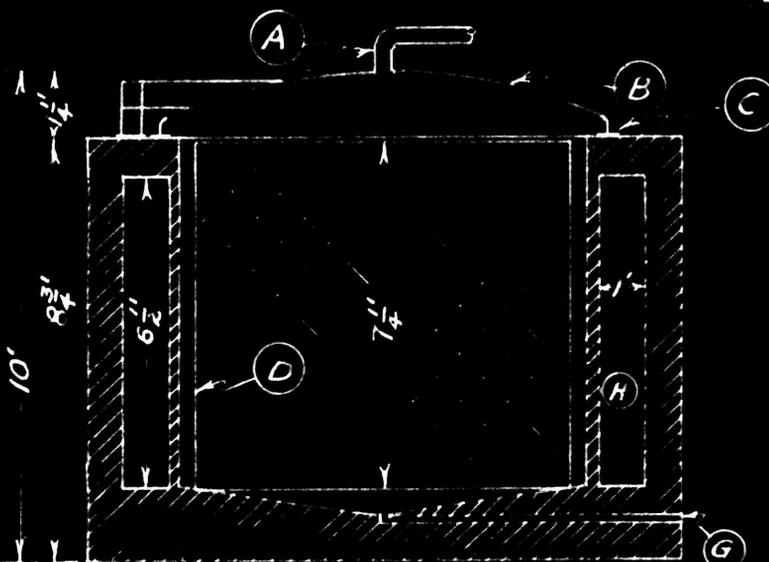
Shape: Cylindrical  
Height:  $4\frac{1}{2}$  ft. with conical bottom  $\frac{1}{2}$  ft. deep  
Diameter: 3 ft.  
Material of construction: cypress,  $\frac{1}{4}$  ft. thick  
Connections: feed at  $\frac{1}{2}$  ft. from bottom edge, exits at tip of conical bottom, at point flush with bottom edge, at  $\frac{1}{2}$  ft. from bottom edge, and at 1 ft. from bottom edge.  
Accessories: 3 ft. long visual level gage to extend from bottom edge of tank upward and located beside outlets.  
Supports: bottom edge of tank 2 ft. above ground level. Tank supported on concrete cribbing,  $3\frac{1}{2}$  ft. x 1 ft. x 1 ft.

B-5 Waste Acid Pump

Capacity: 10 gpm  
Materials handled: acetic acid-methanol mixture  
Head: 30 ft.  
Type: single suction centrifugal pump  
Material of construction: bronze  
RPM: 1450  
Discharge diameter:  $1\frac{1}{2}$  in.  
Motor: furnished with pump  
1 HP, 3 phase, 60 cycle, 220/440 volts, a.c., induction, squirrel-cage, splash-proof, 1750 rpm.  
Equipment available from:  
Motor- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.  
Pump- Worthington Pump and Machy. Corp., Harrison, N.J.  
Number required: one motor and one pump



Plan View



Section A-A

LEGEND

- A-Vapor lead-off line, 2" copper tubing, horizontal, to B-2, Retort Condenser.
- B-Retort cover, 1/4" steel, pressed shape, webbed bracing.
- C-Gasket, asbestos, 1/2".
- D-Pine chip basket, steel wire screen, 1/16" dia., 1/2" opening, 14.08 lb. per sq. ft., braced for 4-point suspension.
- E-Inner retort wall, 2 3/4" thick
- F-Outer retort wall, 9" thick
- G-Creosote outlet, 2" std. iron pipe, horizontal, 1' above G.L.
- H-Heating space, 4 burners spaced equidistantly 2' above G.L., tangential to E, and inclined 10°. Located under I.
- I-Flue, 1'sq., top edge flush with top edge of H, horizontal.

Notes

Fuel oil to be burned in burners.  
 Retort constructed from common fire brick.  
 Number of retorts required - 3

DEPARTMENT OF CHEMICAL ENGINEERING  
 VIRGINIA POLYTECHNIC INSTITUTE  
 BLACKSBURG, VIRGINIA

DESIGN OF A  
**GAS-FIRED RETORT (B-1)**

SCALE: $\frac{1}{4}'' = 1'-0''$	DRAWN BY: WTR	DATE: 7/24/47	DWG. No. 5
CHKD. BY: F.C.	DATE: 8/28/47	FILE No. 539	CASE No. 47
APPRD. BY: F.C.	DATE: 8/6/47		

B-6 Heavy Crudes Pump

Capacity: 10 gpm  
Materials handled: heavy crudes  
Head: 10 ft.  
Type: single stage, single suction, centrifugal, close-coupled, corresponds to Allis-Chalmers Type SS-E  
Material of construction: cast iron  
RPM: 1050  
Inlet and discharge diameters: 1 in., flanged  
Motor: furnished with pump  
     $\frac{1}{2}$  HP, 3 phase, 60 cycle, 220/440 volts, a.c., induction, squirrel-cage, splash-proof, 1750 rpm.  
Equipment available from:  
    Motor- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.  
    Pump- Allis-Chalmers Mfg. Co., Milwaukee, Wisc.  
Number required: one motor and one pump

B-7 Heavy Crudes Storage Tank

Shape: cylindrical  
Height: 5 ft.  
Diameter: 5 ft.  
Material of construction: cypress.  $\frac{1}{4}$  ft. thick  
Connections: feed at 3 ft. above bottom edge, exit at bottom edge  
Supports: bottom edge of tank 1 ft. above ground level and supported on wood cribbing, 6 ft. x  $\frac{1}{3}$  ft. x  $\frac{1}{3}$  ft.

B-8 Light Crudes Pump

Same specifications as B-6

B-9 Light Crudes Storage Tank

Shape: cylindrical  
Height: 4 ft.  
Diameter: 4 ft.  
Material of construction: cypress,  $\frac{1}{4}$  ft. thick  
Connections: feed at 2 ft. above bottom edge, exit at bottom edge  
Supports: bottom edge of tank 1 ft. above ground level and supported on wood cribbing, 5 ft. x  $\frac{1}{3}$  ft. x  $\frac{1}{3}$  ft.

C-1 Light Crudes Fractionator Feed Pump

Capacity: 0.65 gpm  
Materials handled: light crudes  
Head: 40 ft.  
Type: single stage, single suction, centrifugal  
Material of construction: cast iron  
RPM: 1450  
Discharge diameter:  $1\frac{1}{2}$  in.  
Motor: furnished with pump  
1 HP, 3 phase, 60 cycle, 220/440 volts, a.c., induction, squirrel-cage, splash-proof, 1750 rpm.  
Equipment available from:  
Motor- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.  
Pump- Worthington Pump and Machy. Corp, Harrison, N. J.  
Number required: one motor and one pump

C-2 Light Crudes Fractionator

Number of plates: 12  
Plate spacing: 12 in.  
Type plates: bubble cap  
Plate diameter: 10 in.  
Number of caps per plate: 5  
Cap diameter: 3 in.  
Cap spacing (c. to c.): 4 in.  
Cap slot area (total): 7.68 sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 0.5 ft. per sec.  
Feed position: on plates 1, 2, and 3 (from bottom)  
Feed heater: oil immersion type, 5 kw., 230 volts,  
a.c., 32½ in. tube length, 2 heater tubes, corres-  
ponds to Westinghouse style no. 691726  
Creosote exit: below bottom plate  
Pine oil exit: below plates 3, 4, and 5 (from bottom)  
Turpentine exit: below plates 7, 8, and 9 (from bottom)  
Laksol exit: above top plate  
Reflux exit: below top plate  
Reflux ratio: 4  
Steam entrance: below plate 2 (from bottom)  
Materials of construction: steel throughout, welded  
All low-boiling products from the stripping column enter  
the fractionator on the plate above the fraction take-  
off.  
Rates of flow: feed- 4.39 lbs. per min.; Laksol- 0.68  
lbs. per min.; turpentine- 1.18 lbs. per min.; pine  
oil- 0.69 lbs. per min.; creosote- 1.84 lbs. per  
min.; steam (200#)- 0.14 lbs. per min.; reflux- 2.72  
lbs. per min.  
Insulation: 3 in. magnesia (85%)  
Supports: Column resting on 3 ft. reinforced concrete  
Equipment available from:  
Heater- Westinghouse Elec. and Mfg. Co., E. Pitts-  
burgh, Pa.  
Number required:  
Heaters: one

C-3 Light Crudes Fractionator Stripping Column

Number of sections: 2  
Number of plates per section: 4  
Plate spacing: 12 in.  
Type of plates: bubble cap  
Plate diameter:  $3\frac{1}{2}$  in.  
Number of caps per plate: 1  
Cap diameter:  $2\frac{1}{2}$  in.  
Cap slot area (total): 1 sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 2.0 ft. per sec.  
Feed position: fraction from C-2 at top plate and steam at bottom plate of each section  
Exit positions: low-boiling through top plate and high-boiling below the bottom plate of each section  
Materials of construction: Steel throughout, welded  
Rates of flow: feed- 1.18 lbs. per min. (turpentine) and 0.69 lbs. per min. (pine oil); steam- 0.06 lbs. per min. in each section.  
Supports: column resting on reinforced concrete  
Insulation: 3 in magnesia (85%)

C-4 Light Crudes Fractionator Reflux Pump

Capacity: 0.33 gpm  
Materials handled: reflux vapor at approx.  $310^{\circ}\text{F}$ .  
Head: 10 ft.  
Type: single stage, single suction, centrifugal  
Material of construction: cast iron  
RPM: 1050  
Discharge diameter:  $\frac{3}{4}$  in.  
Motor: furnished with pump  
 $\frac{1}{4}$  HP, 3 phase, 60 cycle, 220/440 volts, a.c., induction, squirrel-cage, splash-proof, 1750 rpm  
Equipment available from:  
Motor- Westinghouse Electric and Mfg. Co., E. Pittsburgh, Pa.  
Pump- Worthington Pump and Machy. Corp., Harrison, N. J.  
Number required: one motor and one pump

C-5 Light Crudes Fractionator Reflux Heat Exchanger

Effective length of tubing: 28.1 ft.  
Size of tubing: 1½ in. O. D., 14 B. w. g.  
Tube spacing: 3/8 in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 12 in.  
Condenser type: single or multi-pass. floating head shell, countercurrent flow  
Vapor path: inside tubing, in at 310°F., out at 200°F.,  
0.03 cu. ft. per min. (162.3 lbs. per hr.)  
Cooling medium: light crudes, in at 106°F., out at  
174°F., 0.04 cu. ft. per min. (263 lbs. per hr.)

C-6 Laksol Condenser No. 1

Effective length of tubing: 54.5 ft.  
Size of tubing: ¾ in. O. D., 14 B. w. g.  
Tube spacing: ¼ in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 12 in.  
Condenser type: multi-pass, floating head shell, countercurrent flow  
Vapor path: inside tubing, in at 302°F., out at 80°F.,  
0.015 cu. ft. per min. (40.6 lbs. per hr.)  
Cooling medium: light crudes, in at 70°F., out at  
106°F., 0.08 cu. ft. per min. (40.6 lbs. per hr.)

C-7 Laksol Storage Tank

Shape: cylindrical  
Height: 3 ft.  
Diameter: 2 ft.  
Materials of construction: cypress, ¼ ft. thick  
Connections: feed at 2 ft. from bottom edge, exit at  
bottom edge  
Supports: bottom edge of tank 1 ft. above ground level  
and supported on wood cribbing, 3 ft. x 1/3 ft. x  
1/3 ft.

C-8 Laksol Pump

Same specifications as B-6

D-1 Turpentine Pump

Same specifications as C-4

D-2 Turpentine Fractionator

Number of plates: 8  
Plate spacing: 12 in.  
Type plates: bubble cap  
Plate diameter:  $6\frac{1}{2}$  in.  
Number of caps per plate: 3  
Cap diameter:  $2\frac{1}{2}$  in.  
Cap spacing (c. to c.): 3 in.  
Cap slot area (total):  $3\frac{1}{2}$  sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 0.5 ft. per sec.  
Feed position: on plates 2 and 3 (from bottom)  
Feed heater: oil immersion type, 5 kw., 230 volts, a.c.,  
32 $\frac{1}{2}$  in. tube length, 2 heater tubes, corresponds to  
Westinghouse style no. 691726  
Dipentene exit: below bottom plate  
Pinene exit: below plates 3, 4, and 5 (from bottom)  
Laksol exit: above top plate  
Reflux exit: below top plate  
Reflux ratio: 4  
Steam entrance: below plate 2 (from bottom)  
Materials of construction: steel throughout, welded  
All low-boiling products from stripping column enter the  
fractionator on the plate above the fraction take-off.  
Rates of flow: feed- 1.18 lbs. per min.; Laksol- 0.085  
lbs. per min.; pinene- 0.758 lbs. per min.; dipen-  
tene- 0.337 lbs. per min.; steam at 200# gage- 0.071  
lbs. per min.; reflux- 0.340 lbs. per min.  
Insulation: 3 in. magnesia (85%)  
Equipment available from:  
Heater- Westinghouse Electric and Mfg. Co., E. Pitts-  
burgh, Pa.  
Supports: column resting on 3 ft. reinforced concrete

D-3 Turpentine Fractionator Stripping Column

Number of sections: 2  
Number of plates per section: 4  
Plate spacing: 12 in.  
Type of plates: bubble cap  
Plate diameter: 4 in.  
Number of caps per plate: 1  
Cap diameter:  $2\frac{1}{2}$  in.  
Cap slot area (total):  $1\frac{1}{4}$  sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 1 ft. per sec.  
Feed positions: fraction at top plate and steam at bottom plate of each section  
Exit positions: low-boiling through top plate and high boiling below bottom plate of each section  
Materials of construction: steel throughout, welded  
Rates of flow: feed- 0.758 lbs. per min. (pinene) and 0.337 lbs. per min. (dipentene); steam- 0.038 lbs. per min. (pinene) and 0.030 lbs. per min. (dipentene)  
Insulation: 3 in. magnesia (85%)  
Supports: column resting on 3 ft. reinforced concrete

D-4 Turpentine Fractionator Reflux Pump

Capacity: 0.046 gpm  
Material handled: reflux vapor at approx. 310°F.  
Head: 10 ft.  
Type: single suction, single stage, centrifugal, corresponds to Eastern Engineering Co. type 27208A, model A-1  
Material of construction: steel  
RPM: 1000  
Discharge diameter:  $\frac{1}{4}$  in.  
Motor- connected with pump:  
1/10 HP, 3 phase, 60 cycle, 220/440 volts, induction squirrel-cage, 1000 rpm  
Equipment available from:  
Motor and pump- Eastern Engineering Co., New Haven, Conn.  
Number required: one motor-pump set

D-5 Turpentine Fractionator Reflux Condenser

Effective length of tubing: 1.4 ft.  
Size of tubing: 5/8 in. O. D., 14 B. w. g.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 5 in.  
Condenser type: single pass, floating head shell, countercurrent flow  
Vapor path: outside tubing, in at 310°F., out at 200°F.,  
0.09 cu. ft. per hr. (5.1 lbs. per hr.)  
Cooling medium: water, in at 60°F., out at 100°F.,  
0.095 cu. ft. per hr. (5.9 lbs. per hr.)

D-6 Laksol Condenser No. 2

Effective length of tubing: 6.7 ft.  
Size of tubing: 3/4 in. O. D., 14 B. w. g.  
Tube spacing: 1/4 in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 8 in.  
Condenser type: single pass, countercurrent flow, floating head shell  
Vapor path: outside tubing: in at 302°F., out at 70°F.,  
0.025 cu. ft. per hr. (1.3 lbs. per hr.)  
Cooling medium: water, in at 60°F., out at 100°F.,  
0.20 cu. ft. per hr. (12.4 lbs. per hr.)

D-7 Pinene Condenser

Effective length of tubing: 10.7 ft.  
Size of tubing: 3/4 in. O. F., 14 B. w. g.  
Tube spacing: 1/4 in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 8 in.  
Condenser type: single pass, parallel flow, floating head flow  
Vapor path: outside tubing, in at 329°F., out at 212°F.,  
0.014 cu. ft. per min. (45.4 lbs. per hr.)  
Cooling medium: water, in at 60°F., out at 100°F.,  
0.15 cu. ft. per min. (56 lbs. per hr.)

D-8 Pinene Storage Tank

Same specifications as C-7

D-9 Pinene Pump

Same specifications as C-4

D-10 Dipentene Condenser No. 1

Effective length of tubing: 5.64 ft.

Size of tubing: 3/4 in. O. D., 14 B. w. g.

Tube spacing: 1/4 in.

Tubing material: 0.15 carbon steel

Condenser shell material: cast iron

Type of baffles: orifice

Baffle spacing: 6 in.

Condenser type: single pass, parallel flow, floating head shell

Vapor path: outside tubing: in at 374°F., out at 212°F.,  
0.038 cu. ft. per hr. (20.25 lbs. per hr.)

Cooling medium: water, in at 60°F., out at 100°F., 0.06  
cu. ft. per hr. (32.4 lbs. per hr.)

D-11 Dipentene Storage

Same specifications as B-9

D-12 Dipentene Pump

Same specifications as B-6

### E-1 Autoclave

Shape: spherical  
Diameter:  $4\frac{1}{2}$  ft.  
Material of construction: steel,  $\frac{1}{2}$  in., welded quarter sections  
Connections: Liquid entrance through bottom,  $\frac{1}{4}$  in. std. iron pipe; vapor exit through top,  $\frac{1}{2}$  in. iron pipe. Needle or high pressure valves to be used. Pipe to be welded to shell.  
Heating unit: 25 ft.  $\frac{1}{8}$  in. std. iron pipe containing #20 nichrome IV wire insulated by threading through glass beads  $\frac{1}{3}$  in. dia. Current supplied to be 0.6 kw., 220/440 volts, 3 phase, 60 cycle, a.c.  
Attachments: one 0-150 lb. pressure gage and one thermocouple (iron-constantan). Thermocouple imbedded in vessel wall  $2\frac{1}{2}$  ft. above ground level.  
Insulation: 3 in. magnesia (85%)  
Supports: bottom point of autoclave  $1\frac{1}{2}$  ft. above ground level and supported on 4 legs of 2 in. angle welded to shell and imbedded in 3 ft. reinforced concrete.

### E-2 Autoclave Product Condenser

Effective length of tubing: 10.31 ft.  
Size of tubing:  $\frac{3}{4}$  in. O. D., 14 B. w. g.  
Tube spacing:  $\frac{3}{8}$  in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 6 in.  
Condenser type: single or double pass, countercurrent flow, floating head shell  
Vapor path: outside tubing, in at 680°F., out at 250°F., 6.06 lbs. per min.  
Cooling medium: water, in at 60°F., out at 200°F., 1.25 cu. ft. per min. (78.1 lbs. per min.)

### F-1 Pine Oil Pump No. 1

Same specifications as C-4

F-2 Pine Oil Fractionator

Number of plates: 5  
Plate spacing: 12 in.  
Type plates: bubble cap  
Plate diameter: 4 in.  
Number of caps per plate: 1  
Cap diameter:  $2\frac{1}{2}$  in.  
Cap slot area (total): 1.32 sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 0.5 ft. per sec.  
Feed position: on plates 1, 2, and 3 (from bottom)  
Feed heater: oil immersion type, 5 kw., 230 volts,  
a.c.,  $32\frac{1}{2}$  in. tube length, 2 heater tubes, corresponds to Westinghouse style no. 691726  
Dipentene exit: above top plate  
Pine oil exit: below bottom plate  
Reflux exit: below top plate  
Reflux ratio: 4  
Materials of construction: steel throughout, welded  
Rates of flow: feed- 0.69 lbs. per min.; dipentene-  
0.256 lbs. per min.; pine oil- 0.434 lbs. per min.;  
reflux- 1.024 lbs. per min.  
Insulation: 3 in. magnesia (85%)  
Equipment available from:  
Heater- Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.  
Supports: bottom of column 3 ft. above ground level  
and supported on 4 legs of 3 in. angle imbedded in  
3 ft. reinforced concrete.

F-3 Dipentene Condenser No. 2

Effective length of tubing: 4.76 ft.  
Size of tubing: 3/4 in. O. D., 14 B. w. g.  
Tube spacing: 1/4 in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 6 in.  
Condenser type: single pass. countercurrent flow,  
floating head shell  
Vapor path: outside tubing, in at 374°F., out at  
212°F., 0.256 lbs. per min. (0.279 cu. ft. per hr.)  
Cooling medium: water, in at 60°F., out at 100°F.,  
0.065 cu. ft. per min. (24.5 lbs. per hour)

F-4 Pine Oil Condenser

Effective length of tubing: 14.56 ft.  
Size of tubing: 3/4 in. O.D., 14 B. w. g.  
Tube spacing: 1/4 in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 6 in.  
Condenser type: single or double pass, countercur-  
rent flow, floating head shell  
Vapor path: outside tubing, in at 482°F., out at  
212°F., 0.434 lbs. per min. (0.453 cu. ft. per hr.)  
Cooling medium: in at 60°F., out at 100°F., 1.655 lbs.  
per min. (1.595 cu. ft. per hr.)

F-5 Pine Oil Fractionator Reflux Condenser

Effective length of tubing: 13.73 ft.  
Size of tubing: 1 in. O. D., 14 B. w. g.  
Tube spacing: 3/8 in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 6 in.  
Condenser type: single or double pass, countercurrent  
flow, floating head shell  
Vapor path: outside tubing, in at 390°F., out at 200°F.,  
1.024 lbs. per min.  
Cooling medium: water, in at 60°F., out at 100°F.,  
110.7 lbs. per hr.

F-6 Pine Oil Fractionator Reflux Pump

Same specifications as D-4

F-7 Pine Oil Pump No. 2

Same specifications as B-6

F-8 Pine Oil Storage Tank

Same specifications as B-9

G-1 Reactor

Shape: cylindrical

Height: 5 3/4 ft. with 1/2 ft. round bottom

Diameter: 5 ft.

Connections: dipentene feed at top through iron pipe.  
acid solution feed at top through 2 in. flanged.  
lead-lined (1/4 in. thick) pipe, product drain at bot-  
tom of tank through 2 in. flanged, lead-lined (1/4 in.  
thick) pipe.

Heating: steam at 50 lb. pressure through 3/8 in. lead  
pipe coil in bottom of reactor, length of pipe- 30 ft.

Material of construction: tank made of 1/4 in. steel,  
1/8 in. lead-lined (Te alloy lead).

Supports: bottom of tank 1 1/2 ft. above ground level, 4  
tank supports, 6 in. x 3 in. channel iron, welded to  
reactor shell and imbedded in 3 ft. reinforced con-  
crete.

### G-2 Reactor Pump

Capacity: 10 gpm  
Materials handled: reactor contents  
Head: 20 ft.  
Type: Hydroseal, "A" frame  
Materials of construction: casing- cast iron; impeller, casing housing, suction sleeve, side plate liners- "Maximix" rubber.  
RPM: 520  
Discharge diameter: 2 in.  
Motor: furnished with pump  
     $\frac{1}{2}$  HP, 3 phase, 60 cycle, 220/440 volts, a.c., induction, squirrel-cage, splash-proof, 1750 rpm.  
Equipment available from:  
    Motor- Westinghouse Electric and Mfg. Co., E. Pittsburgh, Pa.  
    Pump- Allen-Sherman-Hoff Co., Philadelphia, Pa.  
Number required: one motor and one pump

### H-1 Settling Tank No. 2

Shape: cylindrical  
Height: 4 ft. with inverted conical bottom  $\frac{1}{2}$  ft. deep  
Diameter:  $3\frac{1}{2}$  ft.  
Material of construction: tank made of  $\frac{1}{4}$  in. steel, 1/8 in. lead-lined (Te lead alloy).  
Connections: feed through open top, acid solution exit at tip of conical section, product exit flush with bottom edge.  
Supports: bottom edge of tank 2 ft. above ground level, 4 tank supports, 6 in. x 3 in. channel iron, welded to tank shell and imbedded in 3 ft. reinforced concrete.

### H-2 Acid Recirculating Pump

Same specifications as G-2

### I-1 Reactor Product Pump No. 1

Same specifications as B-6

I-2 Reactor Product Storage Tank

Shape: cylindrical

Height: 4 ft.

Diameter:  $3\frac{1}{2}$  ft.

Material of construction: cypress,  $\frac{1}{4}$  in. thick

Connections: feed and exit combined at bottom edge of tank.

Supports: bottom edge of tank 1 ft. above ground level, supported on wood cribbing, 3 ft. x 4 in. x 4 in.

I-3 Reactor Product Pump No. 2

Same specifications as C-1

## I-4 Terpeneol Fractionator Feed Heaters

### Terpeneol Side

Effective length of tubing: 39.4 ft.  
Size of tubing:  $1\frac{1}{2}$  in. O. D. 14 B w. g.  
Tube spacing:  $3/8$  in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 12 in.  
Condenser type: multi-pass, countercurrent flow,  
floating head shell.  
Vapor path: outside tubing, in at  $419^{\circ}\text{F.}$ , out at  $100^{\circ}\text{F.}$ ,  
75.0 lbs. per hr. (1.41 cu. ft. per hr.)  
Cooling medium: fractionator feed, in at  $70^{\circ}\text{F.}$ , out at  
 $151.6^{\circ}\text{F.}$ , 4.14 cu. ft. per hr. (292.5 lbs. per hr.)

### Dipentene Side

Effective length of tubing: 206 ft.  
Size of tubing:  $1\frac{1}{2}$  in. O. D., 14 B. w. g.  
Tube spacing:  $3/8$  in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 12 in.  
Condenser type: multi-pass, countercurrent flow,  
floating head shell.  
Vapor path: outside tubing, in at  $374^{\circ}\text{F.}$ , out at  $165^{\circ}\text{F.}$ ,  
3.82 cu. ft. per hr. (202.5 lbs. per hr.)  
Cooling medium: fractionator feed, in at  $151.6^{\circ}\text{F.}$ , out  
at  $296^{\circ}\text{F.}$ , 4.14 cu. ft. per hr. (292.5 lbs. per hr.)

I-5 Terpineol Fractionator

Number of plates: 8  
Plate spacing: 12 in.  
Type plates: bubble  
Plate diameter: 14 in.  
Number of caps per plate: 7  
Cap diameter: 3 in.  
Cap spacing (c. to c.): 4 in.  
Cap slot area (total): 14.5 sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 0.5 ft. per sec.  
Feed position: on plates 1, 2, and 3 (from bottom)  
Feed heater: oil immersion type, 5 kw., 230 volts,  
a.c., 32½ in. tube length, 2 heater tubes, corres-  
ponds to Westinghouse style no. 691726.  
Dipentene exit: above top plate.  
Terpineol exit: above plates 4, 5, and 6 (from bottom).  
Polymer exit: below bottom plate.  
Reflux exit: below top plate.  
Reflux ratio: 3  
Steam entrance: through plate 2 (from bottom).  
Materials of construction: steel throughout, welded  
All low-boiling products enter the column from the strip-  
per on the plate above the fraction take-off.  
Rates of flow: feed- 4.88 lbs. per min.; dipentene-  
3.38 lbs. per min.; terpineol- 1.25 lbs. per min.;  
polymers- 0.25 lbs. per min.; reflux- 10.14 lbs. per  
min.; steam at 200 lbs. press.- 0.30 lbs. per min.  
Insulation: 3 in. magnesia (85%)  
Supports: column resting on 3 ft. reinforced concrete.  
Equipment available from:  
Heater- Westinghouse Electric and Mfg. Co., E. Pitts-  
burgh, Pa.  
Number required: one heater

### I-6 Terpeneol Fractionator Stripping Column

Number of sections: 1  
Number of plates per section: 4  
Plate spacing: 12 in.  
Type plates: bubble cap  
Plate diameter: 7 in.  
Number of caps per plate: 3  
Cap diameter:  $2\frac{1}{4}$  in.  
Cap spacing: 3 in. (c. to c.)  
Cap slot area (total): 1.25 sq. in.  
Liquid seal on plates: 2 in.  
Downspout design: subtended arc type  
Downspout area: equal to total cap slot area  
Allowable tower vapor velocity: 1.0 ft. per sec.  
Feed positions: fraction at top plate and steam through bottom plate.  
Exit positions: low-boiling through top plate and high-boiling below bottom plate.  
Materials of construction: steel throughout, welded.  
Rates of flow: feed- 1.25 lbs. per min.; steam at 200 lbs. press.- 0.30 lbs. per min.  
Supports: bottom of column 4 ft. above ground level, 4 supports, 5 in. x  $2\frac{1}{2}$  in., channel iron, welded to column and imbedded in 3 ft. reinforced concrete.  
Insulation: 3 in. magnesia (85%)

### I-7 Terpeneol Fractionator Reflux Condenser

Effective length of tubing: 100 ft.  
Size of tubing:  $1\frac{1}{2}$  in. O. D., 14 B. w. g.  
Tube spacing:  $\frac{3}{8}$  in.  
Tubing material: 0.15 carbon steel  
Condenser shell material: cast iron  
Type of baffles: orifice  
Baffle spacing: 18 in.  
Condenser type: multi-pass,  $\infty$  unternurrent flow, floating head shell  
Vapor path: outside tubing, in at 390°F., out at 200°F., 10.14 lbs. per min.  
Cooling Medium: water, in at 60°F., out at 100°F., 0.32 cu. ft. per min. (1212 lbs. per hr.)

I-8 Terpineol Fractionator Reflux Pump

Same specifications as C-4

I-9 Terpineol Storage Tank

Same specifications as B-7

Sample Calculations for Equipment Design

Retort Condenser

$$7620 \times 0.55 \times (1000-70) = 3,900,000 \text{ Btu to char wood}$$

$$314 \times 0.45 \times (400-70) = 47,000 \text{ Btu removed with creosote}$$

$$2770 \times 0.242 \times (400-70) = \underline{228,000} \text{ Btu removed with charcoal}$$

$$275,000 \text{ Btu removed}$$

$$3,900,000 - 275,000 = 3,625,000 \text{ Btu in vapors per day}$$

conditions of condenser operation:

vapors enter at  $400^{\circ}\text{F}$ .

vapors leave at 70

water enters at 60

water leaves at 150

therefore,  $dt_m = 74.6^{\circ}\text{F}$ .

$$q = UAdt_m, \text{ assume } (63) \quad U = 105$$

$$3,625,000 = 105 \times A \times 74.6 \times 8 \text{ (8 hours per day)}$$

$$A = 58 \text{ sq. ft. cooling area needed}$$

Sample Calculations (cont.)

Light Crudes Fractionator

Assume light crudes fractions correspond to petroleum fractions as to fractionating characteristics. (53)

Therefore, there will be 4 plates between fractions .

Considering pressure drop per plate, entrainment, plate efficiency, and plate spacing in column performance, the fractionator will have an allowable tower vapor velocity of 0.5 ft. per sec., a plate spacing of 12 in., and a liquid seal on the plate of 2 in. (54).

The column will be run one day for every six days of plant operation.

Amount of feed (per day of plant operation):

Laksol	54.1 lbs.	0.541 mols
Turpentine	94.4	0.692
Pine Oil	55.0	0.366
		<u>1.599</u> mols

Steam for stripping:

Laksol, 54.1 lbs. @ 0.15 lb/5.0 lbs.	Laksol	=	1.62 lbs.
Turpentine, 94.4 lbs. @ 0.25 lbs/5.0 lbs.	Turpentine	=	4.71
Pine Oil, 55.0 lbs. @ 0.45 lbs/5.0 lbs.	Pine Oil	=	<u>4.95</u>
			<u>11.28</u> lbs.
			or 0.627 mols steam

1.599 + 0.627 = 2.226 mols per day of plant operation

PV = nRT

$$14.7 \times 144 \times V = 2.226 \times 1543 \times (302 \quad 470)$$

or V = 1255 cu. ft. per day plant operation  
or 7530 cu. ft. per day column operation  
or 941 cu. ft. per hr. column operation

$$\frac{941}{0.5 \times 3600} = 0.82 \text{ ft. column diameter}$$

Use 10 in. column diameter

Sample Calculations (cont.)

Autoclave

60.6 lbs. pinene to be heated to 680°F. under an allowable pressure of 110 psig.

$$P = (110.0 + 14.7) \times 144$$

$$n = 60.6/136.23$$

$$R = 1543$$

$$T = 680 + 460 = 1140$$

$$PV = nRT$$

$$V = \frac{60.6 \times 1543 \times 1140}{136.23 \times 127.4 \times 144}$$

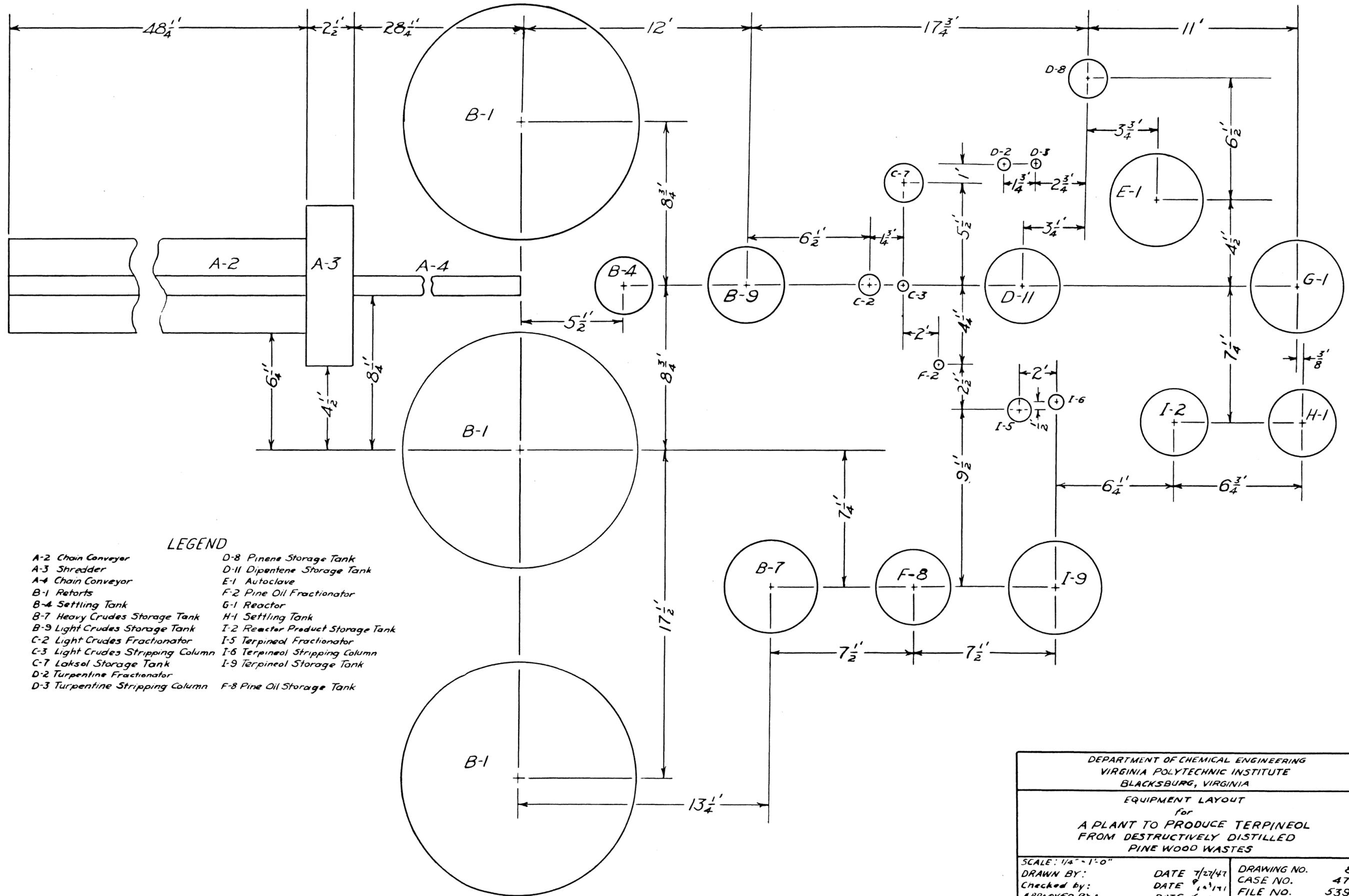
$$V = 43.6 \text{ cu. ft.}$$

if the autoclave is to be spherical:

$$V = \frac{4}{3}\pi R^3 = 43.6$$

$$R^3 = 11.41$$

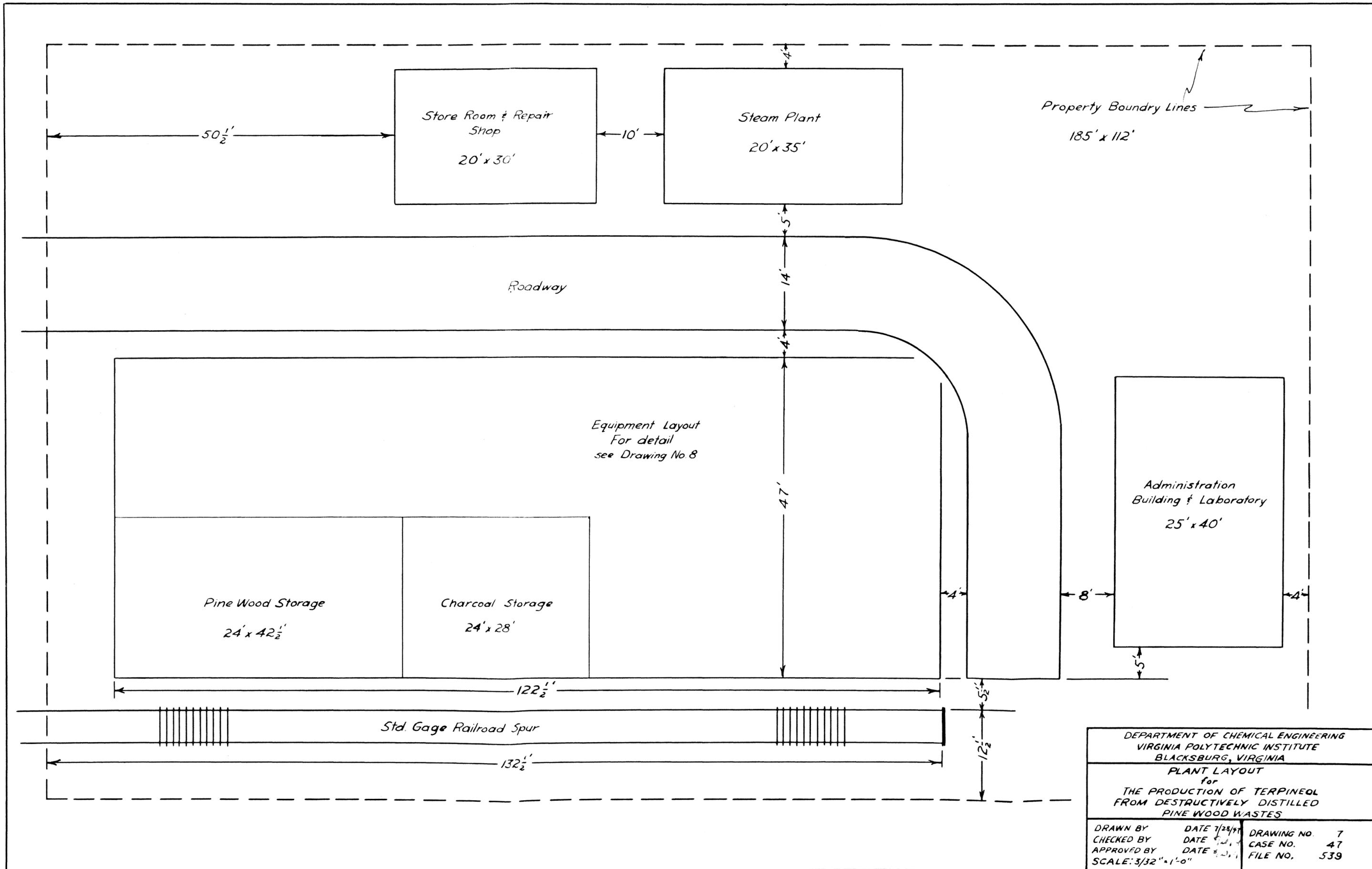
$$R = 2.18 \text{ ft. of autoclave}$$



**LEGEND**

- A-2 Chain Conveyor
- A-3 Shredder
- A-4 Chain Conveyor
- B-1 Retorts
- B-4 Settling Tank
- B-7 Heavy Crudes Storage Tank
- B-9 Light Crudes Storage Tank
- C-2 Light Crudes Fractionator
- C-3 Light Crudes Stripping Column
- C-7 Laksol Storage Tank
- D-2 Turpentine Fractionator
- D-3 Turpentine Stripping Column
- D-8 Pinene Storage Tank
- D-11 Dipentene Storage Tank
- E-1 Autoclave
- F-2 Pine Oil Fractionator
- G-1 Reactor
- H-1 Settling Tank
- I-2 Reactor Product Storage Tank
- I-5 Terpeneol Fractionator
- I-6 Terpeneol Stripping Column
- I-9 Terpeneol Storage Tank
- F-8 Pine Oil Storage Tank

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA			
EQUIPMENT LAYOUT for A PLANT TO PRODUCE TERPINEOL FROM DESTRUCTIVELY DISTILLED PINE WOOD WASTES			
SCALE: 1/4" = 1'-0"			
DRAWN BY:	DATE 7/27/47	DRAWING NO. 8	
Checked by:	DATE 8/1/47	CASE NO. 47	
APPROVED BY:	DATE 8/1/47	FILE NO. 539	



DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
PLANT LAYOUT for THE PRODUCTION OF TERPINEOL FROM DESTRUCTIVELY DISTILLED PINE WOOD WASTES		
DRAWN BY	DATE 7/28/41	DRAWING NO. 7
CHECKED BY	DATE 8/1/41	CASE NO. 47
APPROVED BY	DATE 8/2/41	FILE NO. 539
SCALE: 3/32" = 1'-0"		

### Preconstruction Cost Accounting

#### A. Cost of Raw Materials

1. Pine Wood Wastes, 4 tons/day @ \$10/ton	\$40.00
2. Acetic Acid, glacial, 10 lbs/day @ \$0.083/day	0.83
3. Sulfuric Acid, 66° Be, 10 lbs/day @ \$0.165	1.65
4. Water, processed, 50 lbs/day @ \$0.22/1000 gal	0.01
5. Water, raw, 55,000 lbs/day @ \$0.05/1000 gal	0.03
6. Fuel Oil, 504 gal/day @ \$0.03/gal	15.12
7. Steam, 200 lb gage, 450 lbs/day @ \$0.25/1000 lbs	0.10
8. Electric Power, 72.45 HP x 0.746 x 24 or 1300 kw-hr/day @ \$0.01/kw-hr	13.00
9. Electric Lights, 20 bulbs x 100 watts x 24 or 48 kw-hr/day @ \$0.04/kw-hr	<u>1.92</u>
Cost per day	\$72.66
Cost per year (250 days)	\$18,165.00



C. Equipment Costs

1. Material Storage

<u>No.</u>	<u>Item</u>	<u>Type</u>	<u>Cost</u>
B-4	Settling Tank No. 1	Cyl., cypress	\$75
B-7	Heavy Crudes Storage Tank	" , "	50
B-9	Light Crudes Storage Tank	" , "	50
C-7	Laksol Storage Tank	" , "	50
D-8	Pinene Storage Tank	" , "	50
D-11	Dipentene Storage Tank	" , "	50
F-8	Pine Oil Storage Tank	" , "	50
H-1	Settling Tank No. 2	" , m.s.	125
I-2	Reactor Product Storage Tank	" , cypress	50
I-9	Terpineol Storage Tank	" , "	50
		Total	<u>\$600</u>

2. Material Handling

<u>No.</u>	<u>Item</u>	<u>Type</u>	<u>Cost</u>
A-2	Chain Conveyor	50 ft.(c.to c.)	\$64
A-4	Chain Conveyor	30 ft.( " )	33
B-5	Waste Acid Pump	single suct., centr.	88
B-6	Heavy Crudes Pump	" " , "	50
B-8	Light Crudes Pump	" " , "	50
C-1	L. C. F. Feed Pump	" " , "	65
C-4	L. C. F. Reflux Pump	" " , "	45
C-8	Laksol Pump	" " , "	50
D-1	Turpentine Pump	" " , "	45
D-4	Turp. Fract. Reflux Pump	" " , "	20
D-9	Pinene Pump	" " , "	45
D-12	Dipentene Pump	" " , "	50
F-1	Pine Oil Pump No. 1	" " , "	45
F-6	P. O. F. Reflux Pump	" " , "	20
F-7	Pine Oil Pump No. 2	" " , "	50
G-2	Reactor Pump	Hydroseal, "A"frame	360
H-2	Acid Recirculating Pump	" , "	360
I-1	Reactor Product Pump No.1	sing. suct., centr.	50
I-3	Reactor Product Pump No.2	" " , "	65
I-8	Terp. Fract. Reflux Pump	" " , "	<u>45</u>
		Total	\$1,600

C. Equipment Costs (cont.)

3. Reduction Gears

<u>No.</u>	<u>Reduction</u>	<u>Quant.</u>	<u>Type</u>	<u>Each</u>	<u>Total</u>
A-2	61 to 1	2	Westinghouse DH	\$250	\$500
A-2	2.8 to 1	1	" SH	175	175
A-4	61 to 1	2	" DH	250	500
G-2	2.8 to 1	1	" SH	175	175
Total					\$1,350

4. Motors

<u>HP</u>	<u>No.</u>	<u>Motor</u>	<u>Pulleys</u>	<u>Rails</u>	<u>Each</u>	<u>Total</u>
1/10	2	\$25	*	*	\$25	\$50
1/4	5	40	*	*	40	200
1/2	8	53	\$2	\$6	61	488
1	3	44	2	6	52	156
2	2	60	2	6	68	136
5	1	80	2	6	88	88
50	1	426	**	**	426	426
Total					\$1,544	

\* Not to be used belted

\*\* Not recommended to be used belted

5. Fractionators and Stripping Columns

<u>No.</u>	<u>Item</u>	<u>Size</u>	<u>Cost</u>
C-2	Light Crudes Fractionator	12 plates, 10"dia.	\$650
C-3	L. C. F. Stripping column	8 " , 3 1/2"	400
D-2	Turpentine Fractionator	8 " , 6 1/2"	500
D-3	Turp. Fr. Stripping Column	8 " , 4"	400
F-2	Pine Oil Fractionator	5 " , 4"	350
I-5	Terpineol Fractionator	8 " , 14"	650
I-6	Terp. Fr. Stripping Column	4 " , 7"	350
Total			\$3,300

C. Equipment Costs (cont.)

6. Condensers and Heat Exchangers

<u>No.</u>	<u>Item</u>	<u>Size</u>	<u>Cost</u>
B-2	Retort Condenser	58 sq. ft.	\$615
C-5	L. C. F. Reflux Heat Exch.	11 "	122
C-6	Laksol Condenser No. 1	10.6 "	112
D-5	Turp. Fr. Reflux Condenser	0.3 "	20
D-6	Laksol Condenser No. 2	6.7 "	71
D-7	Pinene Condenser	10.7 "	112
D-10	Dipentene Condenser No. 1	1.1 "	20
E-2	Autoclave Product Condenser	2. "	35
F-3	Dipentene Condenser No. 2	0.9 "	20
F-4	Pine Oil Condenser	2.8 "	35
F-5	P. O. F. Reflux Condenser	3.6 "	45
I-4	Terp. Fr. Feed Heater (Terp.)	15.5 "	250
I-4	Terp. Fr. Feed Heater (Dip.)	80.8 "	1,285
I-7	Terp. Fr. Reflux Condenser	39.4 "	625
Total			\$3,367

7. Miscellaneous Equipment

<u>No.</u>	<u>Item</u>	<u>Cost</u>
A-3	Shredder, 90" x 29" x 84"	\$9,000
B-1	Retorts, 12½' dia. x 8 ¾', 3 @ \$15,000	45,000
B-3	Vapor Separator	50
E-1	Autoclave	400
G-1	Reactor	250
B-1	Hoist	840
Total		\$55,540

8. Instruments

<u>Type</u>	<u>No.</u>	<u>Cost</u>	<u>Total</u>
Flow Meter, recording	17	\$400	\$6,800
Flow Meter, non-recording	6	20	120
Thermometer, record and control	19	150	2,850
Pressure Gage	1	20	20
Float Control Switch	1	20	20
Liquid Level Recorder	1	150	150
Fuel Gage	2	20	40
Total			\$10,000

C. Equipment Costs (cont.)

1. Material Storage	\$ 600
2. Material Handling	1,600
3. Reduction Gears	1,350
4. Motors	1,544
5. Fractionators and Stripping Columns	3,300
6. Condensers and Heat Exchangers	3,367
7. Miscellaneous Equipment	55,540
8. Instruments	<u>10,000</u>

Equipment Basic Cost \$77,301

Installation Costs

<u>Item</u>	<u>Basic Cost</u>	<u>Per Cent</u>	<u>Installation Cost</u>
Tanks	\$1,300	15	\$ 195
Chain Conveyors	97	100	97
Pumps	1,503	10	150
Reduction Gears	1,350	6	81
Motors	1,544	8	124
Fractionators and Stripping Columns	3,300	50	1,650
Condensers and Heat Exchangers	3,367	10	337
Shredder	9,000	15	1,350
Hoist	840	50	<u>420</u>
	Total Installation Cost		\$4,404

C! Total Equipment Cost

Equipment Basic Cost	\$77,301
Installation Cost	4,404
Freight (2% basic cost)	<u>1,546</u>
Total Installed Cost	\$83,251
Accessories (75% installed cost)	<u>62,439</u>
TOTAL EQUIPMENT COSTS (C')	\$145,690

D. Labor and Supervision Costs

<u>Employee</u>	<u>No.</u>	<u>Hrly. Rate</u>	<u>Annual Salary per Employee</u>	<u>Total</u>
Plant Manager	1	---	\$8,000	\$8,000
Wood Handling Area Supervisor	1	---	3,600	3,600
Fractionation Area Supervisor	1	---	3,600	3,600
Reaction Area Supervisor	1	---	3,600	3,600
Chemist	1	---	3,300	3,300
Bookkeeper and Paymaster	1	---	2,700	2,700
Wood Handling Area: Laborers	2	\$1.10	2,200	4,400
Fractionation Area: Laborers	1	1.10	2,200	2,200
Reaction Area: Laborers	1	1.10	2,200	2,200
Maintainance Man	1	1.29	2,580	2,580
Toolroom Worker	1	1.29	2,580	2,580
Watchmen	2	0.80	1,600	<u>3,200</u>
Total Labor and Supervision Costs per Year				\$41,960

E. Fixed Charges

1. Tax	
a. Realty (0.75% of 0.6(B plus C))	\$752
b. Social Security (0.015 of total under \$3,000/yr.)	298
2. Insurance	
a. Extended Coverage (0.5% of 0.9B)	96
b. Equipment (1.0% of 0.66C)	516
3. Depreciation (0.2 of B plus C)	<u>19,706</u>
Total Taxes	\$21,368

F. Working Capital

1. Raw Materials (25% of A)	\$4,452
2. Labor and Supervision (25% of D)	10,490
3. Fixed Charges	
a. Realty Taxes	752
b. Others (25% of E minus realty taxes)	5,152
4. Engineering (10% of B plus C)	9,853
5. Legal Costs	<u>2,500</u>
Total Working Capital	\$33,289

G. Capital Investment

1. Buildings and Land	\$21,225
2. Equipment Costs	145,690
3. Working Capital	<u>33,289</u>
Total Capital Investment	\$200,204

H. Gross Income

1. Charcoal, 346.25 tons/yr. @ \$30.00/ton	\$10,388.00
2. Creosote, 7,670 gal/yr. @ \$0.30/gal	2,301.00
3. Heavy Crudes, 240,550 lbs/yr. @ \$0.025/lb	6,014.00
4. Laksol, 2.235 gal/yr. @ \$0.60/gal	1,431.00
5. Pine Oil, 8,650 lbs/yr. @ \$0.06/lb	519.00
6. Terpeneol, 250,000 lbs/yr. @ \$0.16/lb	<u>40,000.00</u>
Total Income per Year	\$60,563.00

I. Annual Cost

1. Raw Materials	\$18,165.00
2. Labor and Supervision	41,960.00
3. Repairs and Maintenance (5% of B plus C)	4,927.00
4. Marketing and Management (30% of total)	<u>21,618.00</u>
Total Annual Cost	\$86,670.00

### Plant Location

The process of obtaining terpineol from pine wood wastes is one in which the raw material is inexpensive and bulky and is made more compact and given a higher bulk value as a result of processing. This situation will tend to locate the plant as near the raw material source as is possible.

As to the source of pine wood wastes, the state of Georgia at the present time is leading the country in the acreage of pine wood, both living and dead. The labor supply in Georgia would be most desirable because of the number of men in the state who have had previous experience in the processing of pine wood.

Considering Georgia as a whole, power source, supply, and availability would be constant. The power required would either come from the Santee-Cooper Project in South Carolina, or from the Tennessee Valley Authority in Alabama and Tennessee. Water supply, land cost, and plant ordinances would not vary regardless of location in the state. Transportation of the finished products would be the deciding factors in this case.

The markets to be supplied are the eastern and the mid-western sections of the United States. An overseas market might be developed, thus necessitating the plant's access to

a good port. These factors would locate the plant most advantageously near Valdosta, Georgia.

Valdosta is reached by the Georgia Southern and Florida Railway, which would ship through Atlanta, Georgia, to the midwest; by the Georgia and Florida Railway, which would ship through Augusta, Georgia, to the east and north; and by the Atlantic Coast Line, which would ship to Jacksonville, Florida, and Savannah, Georgia, for water transportation.

#### IV. DISCUSSION

##### Results

Destructive Distillation: Three destructive distillation runs, each under a different set of conditions, were made using pine wood wastes reduced in size to approximately four inches in length and one-half inches in diameter. The first two runs, A-1 and A-2, were made in which the pine wood was heated in a closed retort to around 250° C., at which temperature the wood was held, three hours in Run A-1 and one hour in Run A-2. The temperature was then raised until the retort reached 450° C. At this temperature the furnace was turned off and the retort allowed to cool. In Run A-3 the retort temperature was raised at a nearly constant rate of 50° C. per 15 minutes until it had attained 415° C., at which temperature the furnace was turned off. The wood used in the first two runs was a representative sample of the entire tree: it contained parts of the knots, limbs, and stump. The third run, A-3, was made using wood taken only from the stump, hence that wood was richer in terpenes. The different runs were made in the above manner so that the combined condensate from the three runs would be representative of the products of any plan of operation using any combination of pine wood wastes in destructive distillation.

It was found that upon destructive distillation of 100 pounds of pine wood wastes for 4.83 hours at a heating rate of 90° C. per hour and a final retort temperature of 450° C., the product consisted of 36.4 pounds of charcoal, 19.2 pounds of condensate, 2.2 pounds of creosote, and 42.2 pounds of non-condensable vapors, the latter having a density of 3.84 grams per liter.

The presentation of data for the destructive distillation Runs A-1, A-2, and A-3 may be found in Graphs 1 through 6. It will be noted, when referring to these graphs, that several generalizations may be made as to results of operation:

- 1) The vapor temperature lags behind but varies with retort temperature.
- 2) The vapor and condensate rates vary directly.
- 3) The vapor and condensate rates vary with the retort and vapor temperatures.

Decantation. According to the literature, the condensate from destructive distillation, upon settling, separates into three layers: light crudes on the top, then pyroligneous liquor, with heavy crudes on the bottom. In this investigation the condensate from the three destructive distillation runs separated into two layers. Upon batch distillation of these two layers it was found that the

bottom layer consisted wholly of heavy crudes and that the top layer was a mixture of light crudes and pyroligneous liquor. The plant being designed with the intention of facsimilating industrial conditions, necessitated the calculation of the material balance on the basis that the condensate from destructive distillation separated into three layers.

On the aforementioned design basis the condensate from the destructive distillation runs yielded 24 per cent of its weight as light crudes, 10.1 per cent as pyroligneous liquor, and 65.9 per cent as heavy crudes. These data were determined from Runs A-1, A-2, A-3, and A. S. T. M. Distillation of the Top Layer from Destructive Distillation.

Fractional Distillation. The light crudes from decantation were fractionally distilled in a laboratory size fractionation column and the data obtained (boiling point, specific gravity, and refractive index) were plotted against the volume distilled. Graph 8 is the true-boiling-point curve for the light crudes and indicates the presence of one and maybe two definite compounds in large amounts in the light crudes. Graph 9, Volume Distilled vs. Specific Gravity, indicates the presence of a definite compound in the 35-161 milliliter distilled range. This is borne out by Graph 10, Volume Distilled vs. Refractive Index, which

reveals a fairly constant refractive index for the same distilled volume range. From Graph 8 this distilled volume range corresponds to a boiling point range of 135-185° C., and that volume range on Graph 9 corresponds to a specific gravity range of 0.8856-0.9012. This specific gravity and boiling point range completely includes pinene values for the same characteristics. It was considered, therefore, that the portion boiling below this 135-185° C. range was wood naphtha, or Laksol, that this range included pinene and some dipentene, and that the portion boiling above this range contained pine oil and some dipentene. From these conclusions, the following data were calculated: upon distillation of light crudes obtained from decantation, 15.5 per cent of its weight was wood naphtha, 26.8 per cent was turpentine (this term being used to indicate a wide boiling range), 15.7 per cent was pine oil, and 42.0 per cent was creosote, this latter quantity being the residue from distillation.

The turpentine fraction obtained from fractional distillation of light crudes (Run F.D.-1) was fractionally distilled with the results being plotted as before to give Graphs 11, 12, and 13. Analysis of these graphs showed that for a boiling point range of 156.5-174.6° C. the specific gravity and index of refraction corresponded very

closely with those values for pinene. It was considered, therefore, that the portion distilling below the aforementioned temperature range contained wood naphtha and the portion distilling above that temperature range was dipentene. From these conclusions the following data were calculated: upon fractionation of 100 pounds of turpentine (b.p. 155-182° C.) from distillation of light crudes, 7.2 pounds of wood naphtha were obtained with 64.2 pounds of pinene and 28.6 pounds of dipentene. This fractionation was Run F.D.-2.

The pine oil fraction (b.p. 187-261° C.) obtained from fractional distillation of light crudes was distilled with the results being plotted as in Run F.D.-1 to give Graphs 14, 15, and 16. Actually, the data obtained were not intensively studied, the amount of pine oil present being set by the boiling point data given for commercial grades of pine oil. The remainder, or that portion boiling below 200° C., was assumed to be dipentene. Thus, it was calculated that, upon fractionation, 100 pounds of pine oil yielded 37.1 pounds of dipentene and 62.9 pounds of pine oil. The above fractionation was Run F.D.-3.

Chemical Processing. Five general reactions leading to the production of terpineol from pinene were to be investigated: terpineol from pinene, terpin hydrate from pinene,

terpineol from terpin hydrate, dipentene from pinene, and terpineol from dipentene. The reaction, terpineol from terpin hydrate, will be eliminated from discussion as no terpin hydrate was produced or available.

Terpineol from Pinene. The first method tried for producing terpineol from pinene consisted of refluxing pinene with dilute sulfuric acid and glacial acetic acid at a temperature of 93.5-100.0° C., that temperature depending principally upon the concentrations of reactants used. The weight ratio of pinene to sulfuric acid to water was varied from 1:0.326:11.72 to 1:0.326:2.39, with the pinene-acetic acid volume ratio remaining below 1:1 for all runs. The results of this reaction not only gave a low yield (less than 10 per cent) for all conditions; but there were also several products of polymerization formed, as indicated by the high refractive indices and boiling points of the total product. This low yield, along with high polymerization, was considered impractical from a plant design stand-point and this method was abandoned.

The second method for producing terpineol from pinene consisted of mixing pinene with ethyl alcohol (95%) and dilute sulfuric acid. The weight ratio of ethyl alcohol to pinene was never below 1:1. The concentrations of sulfuric acid used were 6 per cent, 14 per cent, 17 per cent, and 48

per cent. The latter concentration resulted in almost complete polymerization of the pinene after one-half hour of mixing and the other concentrations produced less than 8 per cent yield. Time of mixing was varied from one to three hours. Due to this low yield the method was discarded. It had been proven that a sulfuric acid concentration of 50 per cent would result in polymerization of the pinene being treated.

Terpin Hydrate from Pinene. The first method used for attempting to produce terpin hydrate from pinene required that pinene, ethyl alcohol (95%), and hydrochloric acid (sp. gr. 1.16) be allowed to stand together for a considerable length of time. The pinene-hydrochloric acid volume ratio was 1:0.25 and 1:0.35 and the pinene-ethanol ratio was held constant for all runs at 4:1. At the end of 42 hours standing there was no evidence of terpin hydrate crystals in the mixture.

The second method for preparing terpin hydrate from pinene consisted of refluxing pinene with ethyl alcohol (95%) and dilute sulfuric acid (25%). For all runs the volume ratio of pinene to ethanol to sulfuric acid was held constant at 1:1:1. The temperatures of reflux were 25, 50, 75, and 82° C., and the time of reflux was one hour, after which the mixture was allowed to stand for 24 hours. The results

of this reaction were nil and the method of production was abandoned.

Dipentene from Pinene. Pinene was charged into a retort and heated above its boiling point (153-155° C.). Upon arriving at each successive 10° C. interval above 150° C. in the autoclave, the autoclave was opened and a small amount (not over two ml.) of its contents was collected. The autoclave was then closed. These collected samples were analyzed to determine refractive index for each. Six runs (D-1 through 5 and D-7) were made in this manner with the results being plotted as shown in Graphs 17 through 22. In Runs D-1 and D-2 the temperature of the retort did not go above 220° C. and no change was noted in the retort contents. However, in Run D-3 when the temperature was raised to 230° C. there was a change beginning to occur in the pinene. This change, of course, was manifested by change in refractive index from that value of the pinene being heated. In Runs D-4 and D-5 it was noted that the refractive index increased to a maximum of about 1.49 at around 300° C. and then decreased as sharply as it had risen upon the application of more heat to the retort or autoclave. Run D-5, as shown in Graph 21, indicated that upon attaining a temperature of 340° C. the refractive index of the product becomes constant and approximately equal to that of dipentene. This increase and

subsequent decrease in the refractive index of the autoclave contents was assumed to indicate the formation of polymers which fractured due to continued and higher heating of the terpenes.

Additional runs (D-6 through 13) proved that when pinene is heated in an autoclave to a temperature of 330-360° C. the product will have a refractive index and specific gravity nearly equal to that of dipentene (1.4744 at 20° C. and 0.847, respectively). Distillation of the autoclave product revealed that upon heating to 360° C., 100 pounds of pinene yielded 95 pounds of dipentene and 5 pounds of pinene. The time of heating never was longer than one hour and ten minutes.

Terpineol from Dipentene. The method for producing terpineol from dipentene consisted of refluxing dipentene with dilute sulfuric acid and glacial acetic acid. The temperature of reflux was 99.0-109.5° C., depending upon the concentrations of constituents used. The total time of reflux was two hours and six hours. The volume ratio between dipentene and acetic acid was held at around 1:2.5. The weight ratio of dipentene to sulfuric acid to water was varied from 1:0.83:2.0 to 1:0.83:1.0. The latter ratio, which represents a 45 per cent sulfuric acid solution with water, yielded about ten per cent terpineol conversion

upon two hours reflux and 25 per cent after six hours reflux.

Upon distillation of the total product of reflux, the following calculations were made on data collected: to produce 100 pounds of terpineol it was necessary to reflux for six hours at 108.5° C. 359 pounds of dipentene, 19 pounds of pinene, 324 pounds of sulfuric acid (95%), 1025 pounds of glacial acetic acid, and 783 pounds of water. The product of reflux, besides the terpineol, included 256 pounds of dipentene, 14 pounds of pinene, 324 pounds of sulfuric acid, 1025 pounds of acetic acid, 771 pounds of water, and 20 pounds of polymerized terpenes. To obtain these calculations it was necessary to assume that there would be no change in the amount of acetic and sulfuric acid present, that no water was lost to the atmosphere during reflux, and that the pinene present reacted to form terpineol under the same conditions as did the dipentene.

Plant Design and Location. From the foregoing data and results it was decided most practical to produce terpineol by refluxing the product of pinene isomerization. On this basis the necessary equipment was selected and across each piece of equipment a material balance and heat balance was made. Using these balances, each piece of equipment was designed as to capacities, materials of construction, and

most practical operation.

Considering such operational factors as least resistance to flow, related equipment, future expansion, storage of raw materials, and accessibility to the plant, the plant layout was decided upon. It will be noted that the equipment area is totally enclosed, but in equipment design all fractionators, stripping columns, and accessories were designed to operate one day for every six days of plant operation. Thus, future expansion will be handled by merely enlarging a few tanks, an operation facilitated by provision of adequate area.

Upon completion of plant design and layout, the costs of raw materials, buildings and land, and equipment were calculated. These costs were, in turn, used to calculate fixed charges, working capital necessary, capital investment, annual income, and annual cost. It was found that to build the designed plant a capital investment of \$200,204 would be necessary. This plant would cost \$86,670 per year and would return a yearly gross income of \$60,563, thus operating at a deficit of \$26,107.

The location of the plant was decided considering factors of raw materials, labor supply, power supply, transportation facilities, plant ordnances, and land costs. Taking into consideration desirable markets as being in the

midwest and east and possibly overseas, the nearness of the plant to the source of raw materials, the experience of the labor market, and available transportation, it was found most practical to locate the plant near Valdosta, Georgia.

### Recommendations

It was noted in the destructive distillation runs that as the rate of heating was increased sharply and above approximately 3° C. per minute that the non-condensable vapors changed from colorless to a white smoke. This change probably indicated decomposition setting in or possibly the presence of some terpenes in the vapors. To insure collection of all condensate the runs should be made at a temperature rise of not more than 3° C. per minute.

To determine the true products of destructive distillation all runs should be made under optimum conditions. These conditions would include: charging the retort with wood having a length of four inches and a one-half inch diameter, heating the retort at a constant rate of about 3° C. per minute rise, but pausing at 235° C. for one-half hour, and finally shutting down the furnace at a retort temperature of 450° C. This would insure complete carbonization of the wood and the least amount of polymerization of vapors.

Although the boiling point and specific gravity of the samples collected during fractionation seemed to correspond for specific compounds the refractive index was high in every case. Destructive distillation results in the formation of aldehydes, acids, and ketones, which when heated with the terpenes present, promote polymerization of the terpenes.

It was assumed, therefore, that the high refractive indices were the result of the presence of some polymerized material. It is suggested that upon completion of decantation the light crudes obtained be refluxed with about one-tenth its weight of caustic soda for one hour. This procedure will remove the organic impurities present.

In the reaction for producing terpineol from pinene by refluxing with dilute sulfuric acid and glacial acetic acid it is recommended that further study of the reaction be made. The first set of runs should all be refluxed for one hour with a pinene-acetic acid volume ratio of 1:1 or less. The weight ratio of pinene to sulfuric acid to water should be varied from 1:0.326:2.39 to the order of 1:0.5:1.0. Upon determining the ratio yielding the greatest quantity of terpineol, that ratio should be employed in reflux runs varying in time from two to six hours. Possibly the pinene-acetic acid ratio would affect the per cent yield; so, upon determination of optimum conditions from previous runs, this ratio should be varied from 1:1 down to about 1:5.

In the reaction for producing dipentene from pinene the determination of the intermediate compounds formed during isomerization should be made. This would require heating the pinene in an autoclave to about 300° C., removing the autoclave contents, and very carefully fractionating

them. Upon correlation of boiling point, refractive index, specific gravity, and molecular weight data, the compounds present should be readily identified.

The pressure in the autoclave during isomerization of pinene was due only to the pressure of the heated pinene. To ascertain if increased pressure affects the reaction the runs should be made as in this investigation but with the addition of outside pressure, for example, of five pounds per square inch at increasing increments per run.

The reaction for producing terpineol from dipentene should be investigated further. While refluxing at boiling for two hours and holding the dipentene-acetic acid volume ratio at 1:2.5, the weight ratio of dipentene to sulfuric acid to water should be varied from 1:0.25:2.0 to 1:0.83:2.0. Since the weight ratio of 1:0.83:1.0 gave fairly good results, it should be examined by refluxing at boiling for lengths of time between two and six hours and at dipentene-acetic acid volume ratios of 1:2.5 to 1:5.0.

Prior to the design of a plant, the data indicating best yield should be tested on a pilot plant basis. Necessary fractionations should be made using laboratory size columns for better determination of results, but such equipment as the destructive distillation apparatus, the autoclave, and the reactor should be enlarged in size to handle quantities in the order of 50 pounds or more. The pilot plant

stage would enable the investigator to determine, to a closer degree, plant operation, and yields of equipment more duplicating the size of a commercial set-up.

### Limitations

The foregoing section devoted to recommendations for further investigation indicates the extent to which the work should have been carried out.

A more accurate method of determining the volume of non-condensable vapors evolved during destructive distillation should have been devised.

Greater quantities of the reactants should have been used in all reactions. This would have resulted in larger amounts of product which, subsequently, could have been analyzed more thoroughly to determine not only the yield of product but also the actual content of side-products, thus giving a better understanding of the mechanics of the reaction.

Operating instructions for each piece of equipment should have been made, thus serving as a check on the estimates of plant layout, working force needed, and design specifications.

## V. CONCLUSIONS

On the basis of facts developed in the course of this investigation the following conclusions seem to be justified:

1. Upon destructive distillation of pine wood wastes, including stumps, knots, and limbs and reduced in size to four inches in length and one-half inches in diameter, at a retort temperature rate of 90° C. rise per hour, a pause of one hour at 235° C., and a final retort temperature of 450° C., the products obtained were as follows: 36.4 per cent of the weight of pine wood was charcoal, 19.2 per cent was condensate, 2.2 per cent was creosote, and 42.2 per cent was non-condensable vapors.

2. The condensate from destructive distillation, upon settling, separation, and batch distillation, contained 24.0 per cent of its weight as light crudes, 10.1 per cent as pyroligneous liquor, and 65.9 per cent as heavy crudes.

3. The light crudes (b.p. 46-261° C.) from separation were fractionated and found to contain:

a. Wood naphtha, 15.5 per cent of the weight of light crudes, b.p. 69-151° C., sp. gr. 0.8359-0.8696, refractive index 1.4720-1.4794 at 20° C.

b. Turpentine, 26.8 per cent, b.p. 155-182° C., sp. gr. 0.8631-0.8747, refractive index 1.4794-1.4940.

c. Pine oil, 15.7 per cent, b.p. 187-261° C., sp. gr. 0.8905-0.9803, refractive index 1.5020-1.5510.

d. Creosote (residue), 42.0 per cent, b.p. 261° C.-up, sp. gr. 1.229.

4. The turpentine portion from light crudes fractionation was fractionally distilled and found to contain:

a. Wood naphtha, 7.2 per cent of the weight of turpentine, b.p. 137.3-155° C., sp. gr. 0.8700-0.8751, refractive index 1,4800 at 20° C.

b. Pinene, 64.2 per cent, b.p. 156.4-172° C., sp. gr. 0.8650-0.8718, refractive index 1.4802-1.4835.

c. Dipentene, 28.6 per cent, b.p. 174.5-193.0° C., sp. gr. 0.8680-0.8813, refractive index 1.4828-1.5168.

5. The pine oil fraction from light crudes distillation was fractionated and found to contain:

a. Dipentene, 37.1 per cent of the weight of pine oil, b.p. 157.5-200.0° C., sp. gr. 0.8908-0.9096, refractive index 1.4961-1.5050, at 20° C.

b. Pine oil, 62.9 per cent, b.p. 200.0-252.9° C., sp. gr. 0.9380-0.9985, refractive index 1.5157-1.5408.

6. When pinene was charged into an autoclave and heated to 360° C. at a rate of 5° C. per minute the product contained:

a. Dipentene, 95 per cent of the weight of pinene, b.p. 184-187° C., sp. gr. 0.8472, refractive index 1.4748 at 20° C.

b. Pinene, 5 per cent, b.p. 153-155° C., sp. gr. 0.8772, refractive index 1.4644.

7. Upon refluxing for six hours at 108.5° C., 3.59 weight parts of dipentene, 0.19 parts of pinene, 3.24 parts of sulfuric acid (95%), 10.25 parts of glacial acetic acid, and 7.83 parts of water reacted to give the following mixture: 1.00 parts of terpineol, 2.56 parts of dipentene, 0.14 parts of pinene, 3.24 parts of sulfuric acid, 10.25 parts of acetic acid, 7.71 parts of water, and 0.20 parts of polymerized terpenes.

8. A plant designed to produce 100 pounds of terpineol per day would require a capital investment of \$200,204, its operation would cost \$86,670 annually, and the annual gross income would be \$60,563.

## VI. SUMMARY

A plant was designed to produce terpineol from destructively distilled pine wood wastes. The products of destructive distillation were charcoal, creosote, condensate, and non-condensable vapors.

The condensate from destructive distillation settled into layers of light crudes, pyroligneous liquor, and heavy crudes.

Light crudes separated from total condensate were fractionally distilled to obtain wood naphtha, pinene, dipentene, pine oil, and creosote. The first and last two products were end products.

Pinene from fractional distillation was isomerized to dipentene by heating the pinene in an autoclave to 360° C. A conversion of 95 per cent resulted.

The product of pinene isomerization and the dipentene from fractional distillation were refluxed for six hours with dilute sulfuric acid (30 per cent) and glacial acetic acid. Dipentene was 25 per cent converted to terpineol, one per cent polymerized, and 74 per cent unchanged.

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