RESTRICTED

ENCLOSURE (C)

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P I N E R O O T O I L S

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INTRODUCTION

Increase of the production of pine root oil as a fuel source, at present, is most important, and mass production should be carried out by all means, owing to the peculiarity of this source. In order to attain this aim, a wide range of people will be utilized.

In this reference book, the results of experiments and investigations, which were carried out at the First Naval Fuel Depot prior to the beginning of 1945, were edited, with the purpose of spreading the general information to those who were concerned with this matter.

There are several results that need closer investigation but in this reference book only the results obtained will be described.

CHAPTER I

PINE ROOT OIL INDUSTRY, IN GENERAL

A. HISTORY

Pine root oil was the name given to the oily product obtained from the dry-distillation of pine roots. To make pine root oil, there are many methods, i.e., steam distillation, solvent extraction, and exudation, but the dry-distillation method by an iron retort of a horizontal or vertical type was used. The distillates from a vertical iron retort consist of crude pine root oil (light fraction) and pine root tar (heavy fraction); from a horizontal type retort a mixture of pine root oil and tar were obtained at the same time.

The quantities of production in each district of Japan in 1941, are tabulated in Table I(C). From October 1944, an urgent increase in production was planned as a result of the policy of making our fuel supply self-supporting.

The conditions are tabulated in Table II(C).

B. PLAN FOR AN URGENT INCREASE OF PRODUCTION

The execution of the plan for an urgent increase of production was carried out by the system described below.

The contents of this plan were: — every district had its own responsible amount of production; every prefectural Governor was appointed to be the responsible person for the production of pine root oil; the digging of pine roots was carried out by workers from the home office and servicing troops; the dry distillation was carried out by the "Agricultural Economic Society" and the "Self Controlling Association for Pine Root"; the iron retorts and other materials were supplied by the Navy and the Army.

The aims of production during the period from 1 November 1944 to 31 March 1945 were as follows: some hundred million Kan of pine roots (1 Kan = 3.75 kg) and some ten thousand kiloliters of pine root oil. The production of pine roots was already started in the whole country, and, especially in the Northeastern provinces and snowy regions, it was certain that the alloted amount of pine roots would be obtained before the snowy season. At the same time, it was desired to obtain similar production in HOKKAIDO, Korea and Formosa. Especially in Korea "Pine-trunk oil" has been produced since 1944, and now a greater production of pine-trunk oil is also planned.

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As substitute resources for pine roots, pine-trunks, branches, leaves, and Japanese Cypress branches, leaves, and birch-bark, etc. are useful, but they are mentioned in a later chapter.

C. COST OF PINE ROOT OIL

The cost of pine root oil was altered on 2 November 1944, and the new and old prices are shown in Table III(C).

1. Specifications for the oils are shown below.

a. Crude pine root oil

(1) Specific gravity .... 17° Baume at 15°C
Weight of 18 liters .... 17.21 kg
(2) No content of water, other oils and impurities

b. Total pine root oil and tar

(1) Specific gravity .... 13° Baume at 15°C
Weight of 18 liters .... 17.66 kg
(2) Water content .... less than 5%

c. Pine root tar

(1) Water content .... less than 8%
(2) No content of other oils and impurities
(3) Weight for 18 liters should be more than 18 kg

d. Rope tar oil

(1) No content of other oils and impurities
(2) Weight for 18 liters should be more than 18 kg

2. Prices shown (Table III(C) are applicable for the standard oil; viz.,

the standard pine root oil .... 17° Be at 15°C
the standard "total pine root oil and tar" ... 13° Be at 15°C

The price may be increased or decreased, according to the difference of specific gravity from that of the standard oil, ¥1.40 per degree of Baume's hydrometer.

3. The fixed prices of retort and refinery operators shown in the table do not include the price of containers, and the contents only are exchanged at the factories or warehouses of the operators. But the packing charges are paid by the sellers.

4. The fixed prices of regulation organs shown in the table do not include the price of containers and the contents only are exchanged at the factories or warehouses of the operators or sellers. The packing charges are paid by the sellers.

5. When the seller's own drum is used, 80 Sen are added to the above price. If a can is used instead of a drum, ¥1.05 is added to the price.

6. The fixed price for operators shown in the table is limited to the case in which an operator sells his products to the "Japan Regulating Association of Pine-root Oil" or the "National Agricultural and Economical Association". If he wishes to sell to another buyer, the cost must

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be fifty percent of the listed price.

7. This price is also applicable to Japanese Cypress root oil. The ~~items of the cost of pine root dry distillation are as follows:~~

The cost of unearthing roots	26%
The cost for conveyance of roots	44
The cost for roots	6
The cost for chopping roots	20
Miscellaneous	4
Total	100%

D. CONVENTIONAL PRODUCTS AND THEIR UTILIZATIONS

Methods treating pine root oil up to this time, the products obtained and their utilization are as follows:

1. Products from Pine Root Oils

As described above, a vertical retort produces crude pine root oil and tar separately, and a horizontal retort produces "total pine root oil and tar".

Additional flow sheets for refining pine root oil are shown in Figure 1(C) and Figure 2(C).

In the case of the vertical retort, crude pine root oil withdrawn from the end of the condenser tube, and the pine root tar withdrawn from the tar separator, are treated separately. The crude pine root oil is fractionated and the fraction having a boiling point of 130-200°C is called "refined pine root oil" and the fraction above 200°C is called "anhydrous tar". The yields are shown in Figure 1(C).

a. The refined pine root oil is washed with a solution of caustic soda, separating neutral oil and acidic oil, the latter is dissolved in the alkaline solution.

b. The neutral oil is then distilled and the fraction boiling from 140°C to 190°C is called "refined turpentine oil No. 1", the fraction 190-250°C is called "refined turpentine oil No. 2", and the fraction above 250°C is the residual oil.

c. Alkaline solution containing acidic oil is neutralized by the addition of an equivalent quantity of sulphuric acid, thus separating the acidic oil. It is called "wood creosote".

d. By the distillation of pine root tar, "floatation pine oil" having a boiling range of 200-300°C, "rosin oil" or "pine oil" boiling above 300°C and pine root pitch are obtained.

e. Occasionally the mixture of tar and anhydrous tar are called "refined tar" or "rope tar".

However, merchants and refinery operators are averse to the coloring of products and to this matter special attention has been paid, but it appears to have no bad effect on the fuel.

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2. Utilization of Products

Pine root oils have many utilities in the rubber industry, washing and floatation. Furthermore, recently they have been used as motor-fuel, fishing-fuel and lubricating oils.

Utilizations of the primary products of pine root oils are as follows:

a. Crude pine root oil--raw material for producing "refined turpentine oil".

b. Pine root tar--for refining.

c. Total pine root oil and tar--raw material for producing "refined turpentine oil" and others.

d. Pyroligneus liquor--it has not been used, because of its low concentration compared with that obtained from broad leaf trees. However, acetone may be produced from calcium acetate which is obtained by neutralizing it with lime, and boiling it down.

e. Charcoal--the charcoal from pine roots is softer than the ordinary charcoals and contains more gases. It is suitable for quick heating and can be used in tempering, iron works and charcoal gas production. It may also be used as a household fuel, if attention is paid to the ventilation at the beginning of the firing.

f. Wood gas--it is used as fuel for this distillation operation. Utilization of the secondary products of pine root oils are as follows:

Refined turpentine oil No. 1 ...	solvent, washing agent.
Refined turpentine oil No. 2 ...	painting 20%, floatation 80%.
Anhydrous tar	rubber industry 50%, painting 20%, telegraphic wire 10%, horses hoofs 10%.
Creosote	medicine 90%, misc. 10%.
Refined tar oil	rubber industry (high grade), painting, telegraphic wire.
Floatation pine oil	floatation 30%, painting 20%, rubber industry 30%.
Rosin oil	ship's bottom coating, rubber industry, cutting oil.
Pine root pitch	painting 40%, rubber industry 20%, belt wax, cells, etc.
Rope tar oil	rope
Charcoal	about 50% are used as fuels or for distillation of pine roots themselves.

CHAPTER II

DRY DISTILLATION OF PINE ROOTS

A. RAW MATERIALS AND METHOD OF EXCAVATING ROOTS

1. Raw Materials and the Yield of Oil

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Hitherto, pine roots, the trunks of which had been cut down more than ten years ago, were used as the raw material for preparing pine root oil. Such pine trees are called "rich pine".

Its sap-wood had decayed during the lapse of years and its heart-wood was rich in rosin. An example of the relation between the years elapsed and yield of oil is shown below.

Years Elapsed	Yield of Oil, %
10	20-23
7-8	17-18
5-6	15
3-4	12
less than 2	10

When "rich pine" was used we were able to get 4-5 To (7.2-9.0 liters) of pine root oil from 100 Kan (375 kg) of pine roots, but in this plan for increasing production, it was assumed that 2.5 To (4.5 liters) of oil were obtainable from 100 Kan of raw material. Of course, the yield of oil depends not only upon the years elapsed but also on conditions such as, the kind of trees, their ages, and the richness of the soil.

Cypress roots and Thujopsis dolabrata roots are also used, and the yields of oil from them are shown below.

Kind of Trees	Yield of Oil, %
Akamatsu (Pinus densiflora) Kuromatsu (Pinus thunbergii)	11 - 24
Hinoki (The Japan cypress) Hiba (Thujopsis dolabrata)	6 - 10
Todomatsu (Apies sachalinensis) Ezomatsu (Picoa ajanensis)	6

2. Method of Excavating Roots

There are three methods of excavating the roots, i.e. hand-excavation, machine excavation and gun-powder excavation. It is profitable to excavate the roots in red or black soil by hand, those in sand by machine, and big roots by gun-powder. In the case of hand excavation, a hole is dug between the side-roots, using hoes, shovels, axes and saws, big enough to get into to cut off the straight root.

Then the upper side root is cut around the stump, moving the mud into the hole which was dug. On the contrary, if the surrounding side roots are cut off first, the saw is clogged when cutting into straight roots. The expert can excavate 40-70 Kan (150-260 kg) per day. In the case of machine excavation, a root-excavation machine is used. In the case of gun-powder excavation, we use gun powder such as carlit, digging a hole beneath the root-stump which is to be excavated. About 300 grams of gun-powder for a root stump, the diameter of which is about two Shaku (60cm) are used, and the necessary quantity of gun-powder depends upon the softness of the soil.

The root is chopped along the grain and raw material of one Sun (3cm) in diameter and one Shaku (30cm) in length is made and filled in the cage.

In the course of pine root dry distillation, the most laborious work is the excavation and chopping of the roots. In view of the local conditions, raw materials and the present situation, it is difficult to use machine or gun-powder; therefore, it is most important for every person in charge to devise a practical method that is most profitable in each district.

B. DRY DISTILLAT~~ON APPARATUS

The dry distillation apparatus consists of a furnace which heats the raw material from the outside, a dry distillation retort which contains the raw material to be carbonized, a cooling apparatus which condenses the products, and a tank which receives the products.

- Dry Distillation Apparatus
  - Dry Distillation Furnace
    - Furnace
    - Retort
  - Cooling Apparatus
    - Tar Separator
    - Cooling Tubes
    - Cooling Tank
  - Receiving Tank

Many types of apparatus had been already developed all over the country and each of them have their own special characteristics, though with some defects. We cannot get good yields from the clay furnaces. Iron retorts are adopted in general and the vertical type is used in the KANSAI district and the horizontal type in the KANTO district.

The two types of retorts, vertical and horizontal, of course, produce oils having different properties, and requiring different treatment.

It is important to decide upon a standard type of dry distillation apparatus to effect the plan for greatly increasing the pine root oil production and a vertical retort capable of containing about 100 Kan (375 kg) of raw material has been adopted, considering its capacity, efficiency, procedure and required properties.

1. Furnace

Fuel is burnt in the furnace to carry out dry-distillation. The furnaces are classified into several types. Usually it is made of brick, clay and stone, etc., but often only of clay. At any rate, unreasonably built furnaces are not suitable, and if distillation is carried out accidents are sure to occur. The important conditions for furnace construction are as follows.

a. Do not heat by direct fire. Direct firing always superheats the heating surface and sometimes damages the retort.

b. Heating must be uniform. In connection with the above mentioned article, this is important from the standpoint of the yield and the quality of the products. If no attention is paid to this condition, the yield and quality will be poor and the retort will also be damaged.

c. The fuel economy is important. This is important in view of economy and material balance. Huge economical differences are caused depending upon whether the construction technique and management are suitable or not. Thus, the construction must be reasonably designed and skillfully carried on.

The furnace consists of a firing-hole, a grate, a combustion chamber, ~~a chimney and a cleaning-hole, and many designs are reported. The~~ fulfillment of the above mentioned conditions in construction and the economical arrangement of the materials are very necessary.

The important types of the furnaces are shown as follows. They are (1) Kitagawa type which is widely used in the KANTO district and (2) Yamamoto type which is mostly used in the KINKI, CHUGOKU and SHIKOKU districts. The former was designed to circulate the flame and heat the retort uniformly by dividing the combustion chamber into two parts, namely the upper-part and lower-part, while the latter was planned to have an extremely long distance between the firing-hole and the combustion chamber in order to prevent local superheating and to acquire uniform heating by the hot gas evolved. (Figure 4(C).) The standard type is an imitation of the Kitagawa type. At any rate, grates and chimneys are fatal factors for combustion and must be designed with careful considerations.

2. Dry Distillation Retort

There are two types of retorts, vertical and horizontal. The former is again divided into two kinds, one has a bottom, and the other does not.

a. Horizontal retort. This type is suitable for a large scale production, but it is not only difficult to control the temperature but it is also inconvenient for repeated use because of the difficulty of changing the position of the retort after being damaged by super-heating. Moreover, the product is often rapidly carbonized, causing poor yield and quality. The distilled oil is named "total pine root oil and tar" which has to be separated in other plants into "refined pine root oil" and "pine root tar".

b. Vertical retort. Generally speaking, this type is suitable for small-scale production because it is not only possible to control the temperature but also to use the retort again by changing the position of the damaged part. Besides, it suitably carbonizes the raw material, producing a more excellent oil with a better yield when compared with the horizontal type. The distilled oil was easily separated into "refined pine root oil" and "tar".

c. Vertical non-bottom retort. This type was designed to economize material and prevent decomposition by heat which occurred at the bottom. But the gas was apt to leak from the retort causing fire when inadequately constructed. One unit usually consisted of two retorts, each of which could hold about 100 Kan (375 kg) of raw material. The standard type is explained below.

Figure 3(C) shows the sketch and construction of the type which belongs to the vertical-cylinder type. The size of the scale may vary, but the appropriate diameter is two Shaku (60cm) and six Sun (18cm) in view of the carbonization rate which is suitable for ten hours of operation. The larger the diameter the worse the heat-transportation. From this point of view, a folded (4 x 8) steel plate is convenient to make the body, while a (5 x 10) steel plate is too large, since an adequate basket must be put into the oven and cement filled into the clearance, about 1.3 Shaku (1 Shaku = 0.303 m) thick, or the cross section made into an ellipse, the shortest radius being about 2.6 Shaku. A suitable thickness for the oven-wall would be ~~four Bu (12mm), but two Bu (6mm)~~ is enough from the standpoint of its durability. Very thick walls cause bad heat transportation. The part heated directly by the flame is apt to be damaged, and so it is necessary to rotate the retort and change its position at proper intervals. The bottom of the retort has an inclination towards the center, an outlet in the center and contains an inner basket.

3. Cooler

If the distillation can not be carried out smoothly, and no defects in the structure of the furnace are found, bad cooling must be the cause. Therefore, much attention must be paid to the construction of the furnace. Distillation must be carried ~~on at reduced~~ pressure because very high pressure decreases the yield. Then, such constructions which are apt to prevent the flow of the products must be carefully avoided. In fact, the most ideal type is a construction designed suitably for absorbing and removing the inner gases. Much care should be taken to construct the pipe, because great influence on the cooling efficiency is caused by the type of material, the diameters of pipes and the temperature of cooling water. Copper pipes have been employed as coolers, but the shortage of these resources forced us to use substitute-pipes such as porcelain or bamboo. The former predominates in durability but needs careful attention to prevent the leakage of gas, while the latter is less durable and inefficient. The availability of bamboo-pipes with several improvements made on them cover the shortage, and an excellent efficiency comparable with that of copper-tubes, can be obtained.

The following attention must be paid when the bamboo-tubes are used:

a. The end of the pipe must gradually become slender.

b. They must have a small inclination so as to prevent backward flow.

c. It is enough to remove the bamboo-knots by amateur workmanship, and it should be done as in Figure 5(C) and not as in Figure 6(C).

The tar-separator, a large vertical porcelain tube, is packed with broken brick and charcoal, etc. The distilled tar particles collide against the packing, and are then separated and precipitated. A method of connecting the separator with the cooler on the connection tube is shown in Figure 7(C), but a very poor yield was obtained by initial tests, thus requiring improvements as shown in Figure 8(C).

On the other hand, oil is separated from pyroligneous liquor by gravity by installing an oil-separator at the outlet of the cooling pipe.

4. Receivers

Jars and 75 liter capacity barrels are used for receiving tar, "pyroligneous liquor," and crude oil. Care should be taken to prevent the leakage of these liquids.

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5. Fuel and Cooling Water

Fire-wood and charcoal are used for fuel, and wood gas, generated from the retort as by-product of dry-distillation, is sometimes used as an auxiliary fuel. Fire wood that produces long flames is suitable for this purpose. 30-50% of the pine root will be consumed if wood alone is used for fuel. It is said that in a Yamamoto type dry-distillation furnace, in which both charcoal and wood gas are used, the charcoal produced in the retort is sufficient to meet the amount of the fuel necessary for the distillation. As the consumption of fuel largely depends on the construction of the furnace and the method of operation, care should be taken to decrease the fuel consumption.

The consumption of cooling water depends on the construction and capacity of cooling tubes and cooling tank, and the lower the temperature of cooling water the better the cooling effect. The temperature of water at the center of the cooling tank should be below 20°C. Under the best conditions, 27 kl/day of cooling water is efficient for one set of furnaces, but generally the demand for cooling water is larger. The furnace should not be constructed in a place where the supply of cooling water is insufficient.

C. PROCEDURES FOR DRY-DISTILLATION AND EXPERIMENTAL RESULTS

1. The Outline of Procedures

The method of operating the furnace depends on the capacity of the retort. The operation with a 100 Kan (375 kg) capacity retort is as follows.

The inner basket is lifted out (preferably with a pulley) with the charcoal from the previous distillation. The inside of the retort is cleaned, especially the outlet for the oil, because usually it is badly clogged with charcoal dust and pitch. The chopped pine roots are charged into a basket. In the lower half of the basket straight blocks are filled parallel with the wall of the retort, and in the upper half are placed curved and scrap wood. When the "100 Kan standard retort" is used, a smaller hollow basket is placed in the center of the inner basket to obtain perfect carbonization. A fire is then lighted, and before the retort temperature rises, the lid is shut. Uniform heating is essential. At the beginning, the retort is heated strongly until an inner temperature of 280°C is obtained. Then, care is taken not to raise this temperature. At the end of the distillation, it is necessary to make the fire stronger in order to raise the inner temperature to 400°C so as to give complete carbonization. A typical temperature curve of the Kitagawa type dry distillation furnace (standard type) is shown in Figure 9(C). Generally speaking, after two hours of heating, oil begins to distil over and when the inner temperature rises to 270-280°C, tar begins to distil over. By this time heat is evolved by the decomposition wood, and it is necessary to regulate the fire in order not to raise the inner temperature above 280°C. The carbonization degree can be judged by measuring the inner temperature. If no thermometers are available it can be judged by observing the combustion of wood gas. When the inner temperature reaches 270°C, sudden increase in the temperature of the distilled oil takes place. These details can be mastered by repeating the operations, and the operator should earnestly study the peculiarity of his own furnace.

When wood gas is used for the furnace, the firing of the gas must be stopped before the evolution of gas stops. If the firing of the gas is continued, back-firing takes place, sometimes damaging the cooling tube.

2. Outline of the Results of Dry Distillation

a. Details of dry distillation and yield of oil. (cf. Figure 10(C) and Table IV(C). 280-350 kg of pine roots can be charged in this standard retort (the roots contain about 17% H_2O).

After heating 1⅓ hours, pyroligneous liquor begins to distil over from the tar-separator. The rate of water condensation is about 100 cc/min. After 2½ hours of heating, crude oil begins to distil over, drop by drop, floating on the condensed water. A mixture of crude oil and pyroligneous liquor (condensed water) distils over in this form until the temperature of the tar-separator rises to 100°C. This phenomenon is caused by the cooling effect of the tar-separator which is cold at the beginning. It is understood that, even with the same retort, the duration of this phenomenon changes with change in atmospheric temperature during summer and winter. The duration of this state was about 50 minutes in one experiment. Since the tar separator was not insulated with clay, and the atmospheric temperature was about 0°C, this time appears to be rather long. After this period the crude oil distils from the cooling pipe outlet with the pyroligneous liquor, and no oil distils from the tar separator, although at the beginning, a small amount of tar was noticed to be distilled from the outlet for about 30 minutes. This was the heavy fraction remaining in the tubes produced in the previous operation. The specific gravity of the first fraction from the cooling tube is apt to be slightly heavy, since it contains the heavy fractions from the previous operation. During the first 1½ hours, a very light fraction is slowly distilled, but after five hours of heating the specific gravity of the oil becomes heavier and at the same time the amount of distillate (condensed water and crude oil) increases. The amount of distillate per one minute (condensed water and crude oil) is almost constant. In this example the amount of oil was 165cc/min, giving a 25% content of oil in the total distillate. The amount of oil depends on the composition of raw material. Judging from a report made by YAMAMOTO (SHIMANE prefecture), in which the oil content of this distillate was about 20-22%, the heating of the furnace was considered to be too high in this case. In the same report, the total amount distilled during this period was given as 200-220cc. The total amount of distillate depends largely on the amount of pine root charged and is great when small chopped pine roots are used. When pine roots are used, the amount of oil is usually about 20% and it is possible to judge the progress of dry distillation from the amount of oil. The mechanism of dry distillation of wood is not clear, but it is certain that not only steam distillation of turpene oils but also dry distillation or carbonization of cellulose, lignin, rosin and saccharoid take place, accompanied by heat evolution. It is necessary to regulate the firing during this period. It is said that the slower the distillation and the longer the time the better the quality and yield of oil. After this period, the amount of pyroligneous liquor and oil distilled suddenly decreases and then stops. In the case of this experiment, the time required from the beginning of heating until the end of distillation was about 9½ hours, but if 300 kg of pine roots were packed in the retort it would be best to raise the temperature of the slow and smooth operation for 13 hours. In the case of actual production of pine root oil, the fireman has to work on chopping pine roots and make an appa-atus for the next distillation, and distillation is stopped after 10-11 hours. Therefore ideal operations cannot be realized.

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After distillation of the crude oil from the tar-separator ceases, tar begins to distil from the tar-separator, with pyroligneous liquor. After 2½ hours the distillation of tar becomes violent, and from this time almost tar alone is distilled from the tar-separator. From the outlet of the cooling tube, non-condensable "wood gas" (a mixture of CO_2, CH_4, C_2H_4, H_2 etc.) is exhausted. The outflow of tar continues violently (in this case 330cc/min.), but decreases suddenly before the outflow of crude oil decreases, and ceases after the outflow of crude oil stops. The end of the operation can be told by this fact. The yield of oil is usually about 20% of the pine roots and, if oil-rich roots are used, it increases up to 25%. The ratio of crude oil to tar was 1:1.1 in this case, but it was 1:1.9 in another case. The average ratio seems to be about 1:1.3. The specific gravity and the distillation curves for the distillate are shown in Figure 10(C).

b. Firing method and relation between water content of raw material and fuel consumption. A large quantity of fuel is used at the beginning and later its consumption may be decreased gradually. As soon as the evolution of wood gas begins, it may be used as the main fuel extremely diminishing the amount of charcoal and fire wood. In the last stage, some solid fuel is added to obtain perfect carbonization of raw material in the retort. The standard amount of dry fire wood used is as follows:

Let the operation period be 11 hours. Then about 63 kg of wood for the first two hours is necessary. For the next five hours, 19 kg of wood and some fragments of pine root, which are added to prevent the temperature decrease, are used. The gas evolved from the retort by this time is also used. For the next three hours, it is sufficient to use only the gas to maintain the furnace temperature, as the heat of carbonization also supports the temperature. For the last one hour, 37 kg of fire wood is used. The total amount of dry fire wood is about 133 kg but can be economized by using the charcoal produced. Table VII(C) shows an example of using fire wood and charcoal together.

The relations between the water content of raw materials, the center temperature of the retort and the fuel consumptions are shown in Figure 11(C). When the water content is rich, the temperature in the still can not rise easily and a large amount of fire-wood is necessary. Since the yield of oil is the same as in the standard case, this causes a great inconvenience as the operation time is prolonged. When an empty basket is inserted in the middle of the retort, the speedy rise in temperature is achieved. From Figure 11(C) a 5% water content of raw material appears to be advantageous, as it indicates an extremely short operation time, and a very small amount of fuel consumption, but the distillates are apt to distil over violently, causing bumping in the tar-separator and rending the firing control difficult. To prevent such troubles, water must be added to the raw material.

c. Temperature distribution in retort. Table V(C) and Figure 12(C) show the temperature variation with time in the retort. In this case, "Pinus thunbergii" trunks with water contents of 35% were charged in a standard furnace, and no center basket was used. Although this furnace was not perfectly dried, and the raw material had a high water content, the outline of temperature variation may be noted as a reference.

The variation of isothermal lines in Figure 12(C) were drawn by assumption, summarizing the measured temperature in one retort and the carbonization degree of pine roots in another retort.

The highest temperature of the retort is in the middle outside part and the temperatures of the upper outside part and the lower outside part are lower. It is clear that the temperature of the middle lower part is the lowest because non-carbonized matters frequently remain in this part. When material with lower water content, such as pine roots are used, the temperature increase in the middle part is quicker, producing a more uniform temperature distribution than shown in the figures.

D. CONDITIONS FOR ESTABLISHING PINE ROOT DISTILLATION UNITS

Following conditions must be satisfied for establishing pine root distillation units.

1. Pine roots must be abundant in the neighborhood.
2. Transportation must be convenient.
3. Cooling water must be readily obtainable. About 13.5 kiloliters of cooling water are necessary for a standard still.
4. Soil must be dry.
5. Employees must be readily available.
6. Plants must be safe from fire.
7. Water drainage must be convenient.

E. PRODUCTION OF CA-ACETATE FROM PYROLIGNEOUS LIQUOR

The pyroligneous liquor obtained with the crude pine root oil is neutralized with lime water. At the same time, utmost care must be taken to avoid the existence of excess lime because the quality of the calcium acetate will become poor, even if more pyroligneous liquor is added to neutralize the excess lime. Litmus papers are very useful for this operation.

The boiling and drying of the neutralized liquid are carried out in the apparatus shown in Figure 13(C). More neutralized liquid is added after boiling down and yellow or brown crystals are formed on the surface. They are dried at a temperature below 150°C, partial decomposition of the crystals occur lowering the yield of acetone.

CHAPTER III

PROPERTIES AND CONSTITUENTS OF DRY-DISTILLATION PRODUCTS FROM PINE ROOTS

By dry distillation of pine roots, oil, pyroligneous liquor, and wood gas are produced. Oil is the main product.

Pine root oil is classified as: "crude pine root oil", "pine root tar" and "total pine root oil and tar". The former two are obtained from vertical retorts and the latter from horizontal retorts.

An example of their properties are shown in Table VI(C).

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A. CRUDE PINE ROOT OIL

Crude pine root oil is a light brown liquid and has a specific gravity of 0.95-0.99. Its properties and constituents vary with the conditions of dry distillation.

The results of the examination on the constituents of pine root oil are as follows:

1. Neutral Constituents

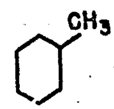
Crude pine root oil obtained from "Kuromatsu" was fractionated, and after treating with sufficient alkali the constituents were examined.

The constituents and their percentage to total crude oil are summarized as follows:

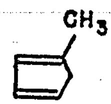
Note: * Sign indicates main constituents.

a. Light fraction (Initial drop-150°C) (3%-8%).

* Toluene (B.P. 110°C)



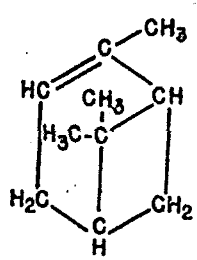
* Sylvene



Sylene	Furan	Furfural
Diacetyl	$(CH_3CO)_2$	
Acetylpropionyl	$(CH_3CO.C_2H_5CO)$	

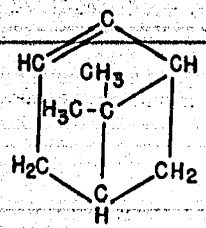
b. Terpene fraction (150-170°C) (40-70%)

* 1-a-Pinene (B.P. 155-156°C)



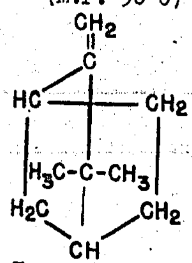
ENCLOSURE (C)

* Limonene and Dipentene (B.P. 175°C)

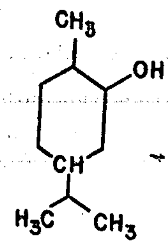


* Camphene

(M.P. 50°C)

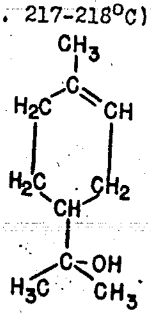


p-Thymol



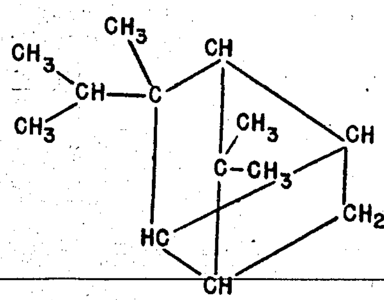
c. Terpenic alcohol fraction (200-230°C) (small amount)

* a-Terpineol (B.P. 217-218°C)



d. Sesquiterpene fraction (110-120°C/8.5mm Hg) (10-30%)

* d-Longifolene (B.P. 149-151°C, 36mm Hg).



ENCLOSURE (C)

e. Higher terpene fraction (120°C, 3mm Hg) (10-30%)

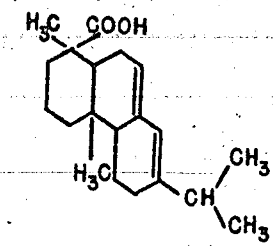
* Abietine ($C_{19}H_{30}$ or $C_{19}H_{28}$), constituent of rosin oil.

* Retene (M.P. 98°C), constituent of paraffinic crystal

f. Residual fraction

(1) Main constituent is abietic acid

* Abietic acid (M.P. 158°C)



(2) Aldehydes, Ketones. These were extracted by a Sulphite solution from crude pine root oil.

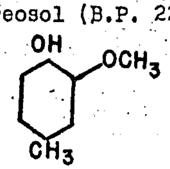
Acetaldehyde CH_3CHO and acetone $CH_3.O.CH_3$ are probably present.

(3) Carboxylic acids. The acids were extracted by a sodium carbonate solution from the solution after extracting aldehydes and ketones.

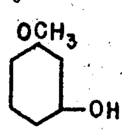
Formic acid (B.P. 100.6°C)
Propionic acid C_2H_5COOH (B.P. 140°C)
Isobutyric acid $(CH_3)_2CH.COOH$ (B.P. 154°C)
Valeric acid C_4H_9 COOH (B.P. 185°C)
Capronic acid $C_5H_{11}COOH$ (B.P. 205°C)
and other higher carboxylic acids.

(4) Phenols. These were extracted by a sodium hydroxide solution after removal of carboxylic acids.

Creosol (B.P. 222°C),



Guajacol



Other mono-phenols are also present.

ENCLOSURE (C)

B. PINE ROOT TAR

Pine root tar is a black, viscous liquid and has a density of about 1.06. Pine root tar consists mainly of cracked resin products and terpene compounds with a small amount of cracked lignin products. Its main constituents are probably abietic acid and its homologues and polymers of higher terpenes.

C. PYROLIGNEOUS LIQUOR

Pyroligneous liquor is a reddish brown liquid, having density of 1.025-1.03. Most of the liquid is water, containing the substances listed below.

1. Soluble Tar (2-9%)

This is the cause of the coloring and can be extracted by solvents. It probably consists of high polymers of aldehydes and ketones.

2. Organic Acids (3.5-4%)

These were determined as acetic acid. Formic acid and other higher carboxylic acids exist too.

a. Acetone (0.2%)
b. Methanol (0.1-0.6%)
c. Formic aldehyde and ketones.

D. WOOD GAS

The composition is tabulated below.

CO_2	40%
CO	25%
CH_4	15%
C_nH_{2n}	3%
O_2	2%
N_2	15%

Calorific value is greater than 2,000 calories.

CHAPTER IV

TREATMENT OF PINE ROOT OIL

The properties of pine root oil have been described in Chapter III and the main constituent of the fraction below 300°C in "terpene", while that of the fraction above 300°C is "abietine". It is, therefore, possible to obtain a high quality aviation gasoline from pine root oil by suitable treatments. As this oil contains a large amount of acidic constituents and has a corrosive effect on metal, suitable pretreatments are necessary. It was clarified by the investigations in this laboratory that the following treatments were very effective.

ENCLOSURE (C)

A. PRETREATMENT

1. Pretreatment

Corrosive acids in pine root oil exist in the fraction below 250°C and the acidic constituents in the fraction above 250°C are comparatively harmless. Pretreatment is carried out as follows. (cf. Table VII(C).)

a. Crude pine root oil. An equivalent amount of water or 0.4% lime-water is added to the oil at about 60-80°C and the mixture is stirred. The oil and water are separated by gravity.

b. Total pine root oil and tar. An equivalent amount of 3% NaCl-solution of 1% lime-water added to the oil at 80°C and the mixture is stirred. The oil and water are then separated by gravity.

c. Pine root tar. Tar is distilled directly in cylindrical stills and the fraction below 300°C is mixed with pine root oil, and treated and refined together.

2. Distillation Method

The following cuts were obtained by distilling the pretreated oil.

a. Fractions below 200°C were used for catalytic reforming.

b. Fractions below 300°C were used for hydrocracking. If catalytic reforming is being carried out, fractions between 200-300°C are adopted as material for hydrocracking. Researches are being made on direct hydrocracking on the oil without previous treatment.

c. The pine root tar fraction above 300°C and pretreated oil are distilled in a coking-still, producing heavy oil and cokes.

d. Local apparatus should be utilized as distilling stills except those specially described, but it is right to use cylindrical types, particularly when pine root tar, and "total pine root oil and tar" are used.

B. METHOD OF MANUFACTURING AVIATION GASOLINE

1. Catalytic Reforming Method

Fractions up to 200°C can be reformed over catalysts producing aviation gasolines.

2. Hydrocracking Method

A fraction boiling up to 300°C or boiling from 200°C to 300°C, in case it is necessary to operate catalytic reforming in parallel, can be converted to aviation gasoline by hydrocracking. A diagram showing treatment of pine root oil is given in Figure 14(C).

Aviation gasoline can be obtained in high yield, while heavy oil can be obtained by suitable treatment of heavier components. It is expected that light oil can be obtained from the 200-300°C cut.

Oils from pine root oil are characteristic in the point that they mostly contain "naphthenes".

ENCLOSURE (C)

CHAPTER V

SUBSTITUTE RESOURCES FOR PINE ROOT AND METHODS FOR THEIR UTILIZATION

As pine root is a limited resource, it cannot be expected to last for a long time. Therefore, it is very important to utilize other resources.

Those investigated or previously used are listed below.

1. Acerose trees
   a. Trunks b. Branches c. Leaves
2. Broad leaved trees
3. Pine resin
4. Pulp and sawdust
5. Waste gas of charcoal oven

A. UTILIZATION OF ACEROSE TREES

1. Utilization of Trunks

Pine trunks are poor in oil compared with pine roots, but they are a promising abundant source. At present, in our laboratory experiments on dry distillation are being carried on by the standard furnace. Typical results are shown in Table VIII(C).

In general, the yield of tar is about 5% and the older the age of the tree, the greater was the yield. The age is required to be over 50 years at least.

Trunks of incomplete growth are rich in resin and are regarded as unsuitable for building material. The raw material must be dried until the water content is less than 20%. Characteristics of dry-distilled oil are indefinite and an example is shown below.

General Characteristics

Reaction	acidic
Specific gravity (d_4^{25})	1.012
Viscosity (R-1 30°C)	169.2
Freezing point	140°C
Flash point	57.0°C
Carbonizing matter	2.45%
Ash	0.16%
Water	4.3%
Impurity	trace

Characteristics of Partial Distillation

Initial boiling point	85.0°C
5%	98.0°C
10%	170.0°C
20%	191.0°C
30%	215.0°C
40%	236.0°C
50%	254.0°C
60%	272.0°C
70%	303.0°C
80%	329.0°C

ENCLOSURE (C)

90%	334.0°C
Dry point	339.0°C
Total % of distillate by volume	91.0%

2. Utilization of Branches

a. Dry distillation of Japanese cypress. The part of the branch near the trunk contains the greatest amount of resinous matters in acerose trees. The part of the branch about 50cm from the trunk is similar to pine root, and the upper parts contain only a small amount of resin. The results of dry distillation of Japanese cypress at "Kisoagematsu Essential Oil Factory of the Imperial Forest Bureau" (in 1942) are shown in Table IX(C).

b. Dry distillation of pine branches. In Korea, pine branch oil is being produced by low temperature dry distillation of pine branches. This method has been made by special clay charcoal kilns. The average yield is 5-6% and in 1943, 800 tons/year were produced, but in 1944 an urgent increase in production to 18,000 tons/year was planned.

3. Utilization of Leaves

Leaves of acerose trees contain essential oil, which are obtained by solvent extraction or steam distillation. Dry distillation of leaves is not suitable.

a. Extraction method. Oil can be obtained by extraction of acerose leaves with solvents, such as alcohol, ether, etc. When air-dried leaves of cyptomeria were extracted with alcohol by Sexlehet's method at the "Fermentation Research-laboratory of the Munitions Ministry", extracted oils were obtained in yields of about 15%. The extracted oil was a dark brown, viscous, and tarlike matter.

Experimental results with pine, cyptomeria, and Japanese cypress are shown in Table X(C).

Alcohol, methyl alcohol, acetone and turpentine oil may also be used as solvents.

Hydrogenated oil from this extracted oil is separated into gasoline and heavy oil, and octane number and cetane number of each oil are shown in the following tabulation.

Gasoline

Boiling range	68-220°C
Yield	30%
Appearance	orange brown, transparent
Octane number	76

Heavy Oil

Boiling range	221-360°C
Yield	60%
Appearance	violet
Cetane number	20

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b. Steam distillation method. This method has been used for manufacturing essential oil. Only essential oil is obtainable by this method, and it is suitable for small amounts unfavorable for dry distillation. The yield is very poor, below 1%.

Silver-fir leaves (Pricea ajanensis) and Todo-fir leaves (Abies sachalinensis) were utilized in HOKKAIDO, while Japanese cypress leaves were treated in the KISO-district.

Drums with coolers are sufficient for distilling apparatus.

B. UTILIZATION OF BROAD-LEAVED TREES

1. Dry Distillation of Trunks

Broad-leaved trees were formerly dry-distilled to obtain charcoal and pyroligneous liquor, but now they are treated to obtain charcoal only. Dry distillation to obtain tar will be described here and charcoal manufacturing in a later chapter.

a. Catalytic dry distillation method. Investigation was made with the co-operation of the Tokyo Examination Office of the Imperial Forest Bureau, and the Physical and Chemical Laboratory. As oils obtained from broad-leaved trees belong to so-called heavy oil fractions and have poor utilization, we must construct a catalyst room between the dry-distillation retort and cooler, and decompose the heavy oil catalytically to obtain light oil and "acetonize" acetic acid in the pyroligneous liquor.

The catalyst is pressed in tablets and packed in the catalyst room. The composition of the catalyst is as follows.

Ash	3.0
Clay	1.0
Cement	1.0
Mg-carbonate	0.2

About two times the yield of light oil is obtained by this method as compared with the simple dry distillation method. The properties are as follows.

(1) Light oil (Fraction boiling up to 220°C and washed by alkali)

Boiling range	70-220°C
Specific gravity	0.900-0.968 (20°C)
Refractive index	1.4170-1.5189 (n_D^{20})
Octane number	83

This yellow oil is easily self-oxidized but can be stabilized by hydrogenation.

(2) Heavy oil (220-250°C). This yellowish-red, unstable oil, having a peculiar smell, and an easily self-oxidizing tendency, becomes brownish-black and viscous when exposed in the air.

(3) Heavy oil (250-300°C). A brownish-black and viscous oil, showing yields from various trees as given in Table XI(C).

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2. Dry Distillation of Birch-Bark (cf. Figure 15(C).)

The results of the researches at the Central Laboratory of the Southern Manchurian Railway Corp. are described in this section.

The outer bark of the birch (produced in Manchuria) was heated at the rate of 17°C/10 min for five hours. The outflow of the oil began at 200°C, and stopped completely at 500°C. The outflow of tar was most rapid at 300-400°C. Yields of the distilled products are shown in Table XII(C).

The obtained tar is greenish-brown and has a fluorescence.

Specific gravity (d_4^{20}) 0.952
Viscosity ...... 12.88 (The specific viscosity to water at 30°C)
Freezing point .... 3°C
Acidity .... 0.32 N (Titrated with N/10 NaOH solution)

The properties of the neutral distillate are shown in Table XIII(C).

The water solution was light yellow at the beginning but gradually changed to a reddish-brown color and finally to black. The specific gravity was 1.018 (d_4^{20}), acidity 1.02 N (6% as CH_3COOH).

Dry distillation experiments on birch-bark carried out in the laboratory of this Depot show the following results. The distillation of oil began at 200°C and it was most violent at 335-400°C, and the yield of tar was far better than that of pine-root.

The amount of bark obtained from birch-trees is 12.5 kg per 1 m^3 of wood according to reports from the gathering-district.

C. DRY DISTILLATION OF PINE-RESIN

Demand and supply of pine resin in the Far East is given in Table XIV(C) and the production prospect is nil.

The results of dry distillation of pine resin with clay are shown in Table XV(C).

D. UTILIZATION OF PULP AND SAW-DUST

1. Utilization of Pulp Factories

When the liquid from a pulp digester is cooled, the essential oil fraction of pulp wood can be recovered. When the waste solution of pulp is dry-distilled, tar can be recovered. Reported results from the Laboratory of the Imperial Forest Bureau at TOKYO, are next shown in Table XVI(C) (dry distilled with catalyst).

2. Dry Distillation of Saw-Dust

Dry distillation of saw-dust or waste wood in saw mills is a possible fuel source. But saw-dust is hard to distill, and a special furnace is necessary, such as laminar dry distillation. An effective distillation method must be studied in the future.

ENCLOSURE (C)

E. UTILIZATION OF WASTE GAS FROM CHARCOAL OVENS

Up to this time, the gas from charcoal ovens was scarcely utilized, and it was exhausted into the air. But a large amount of calcium acetate can be produced with simple equipment. The apparatus with which pyroligneous liquor is obtained from the smoke from the oven, is shown in Figure 16(C).

While the smoke is still white, the damper must be fully opened, so that combustion in the furnace is effective. When the smoke changes to yellow, the damper is slowly closed. After carbonization is carried on sufficiently, the smoke changes to blue, and the damper is tightly closed. The pyroligneous liquor is conducted to a receiver. At this moment, if enough care is taken in ventilation, the amount of charcoal will never be lacking and its amount will not decrease. Calcium acetate is obtained from this pyroligneous liquor by the following process: separation of tar, neutralization with milk of lime, and concentration.

The assumed yields of by-products obtained per year from the waste gas of a charcoal oven, are as follows.

White charcoal	984,200,000 kg
Black charcoal	1,828,100,000 kg
Total	2,812,300,000 kg

1. In the case of collecting pyroligneous liquor from a white charcoal oven.

Calcium acetate		118,125 tons
As CH_3COOH -	pure	56,101 tons
	commercial	19,341 tons
As acetone		30,902 tons
Wood tar		24,609 tons

2. When pyroligneous liquor is collected from a black charcoal oven.

Calcium acetate		137,109 tons
As CH_3COOH -	pure	65,118 tons
	commercial	22,449 tons
As acetone		35,868 tons

3. Wood tar can also be recovered from a black charcoal oven by adding special apparatus.

Wood tar	44,844 tons

Total

Calcium acetate		255,234 tons
As CH_3COOH -	pure	121,219 tons
	commercial	41,790 tons
As acetone		66,770 tons
Wood tar		79,453 tons

ENCLOSURE (C)

Table I(C)
PRODUCTION OF PINE ROOT OIL IN 1941

Name of Prefecture	Vertical Type		Horizontal Type	Numbers of	
	Crude pine root oil (kg)	Pine root tar (kg)	Total pine-root oil and tar (kg)	Retort operators	Retorts
Aomori	—	—	—	42	4
Iwate	1,350	5,505	—	4	6
Miyagi	25,250	22,020	1,530	3	16
Akita	—	—	180	1	2
Yamagata	8,988	7,944	14,960	11	28
Fukushima	7,482	33,791	6,625	4	6
Ibaragi	16,810	5,560	104,220	13	21
Tochigi	34,030	4,800	16,160	8	19
Gumma	6,546	5,305	18,600	7	18
Saitama	—	—	4,800	1	1
Chiba	313,174	66,766	337,606	76	98
Kanagawa	—	5,625	—	3	7
Niigata	850	—	—	3	25
Ishikawa	34,800	51,227	—	5	15
Fukui	122,468	373,320	—	14	39
Yamanashi	433,547	648,212	128,225	16	44
Nagano	68,040	157,140	105,300	25	34
Gifu	82,446	109,375	—	5	22
Shizuoka	63,137	20,329	105,219	6	41
Aichi	116,652	157,329	46,620	3	24
Mie	40,460	11,200	—	4	11
Shiga	9,420	11,970	22,140	5	15
Kyoto	248,390	142,290	250	15	63
Osaka	25,347	48,996	—	5	21
Hyogo	57,307	69,012	—	18	61
Nara	167,130	21,000	—	9	25
Wakayama	63,380	117,047	—	9	27
Tottori	313,820	587,880	21,000	18	67
Shimane	34,200	68,400	—	53	127
Okayama	68,449	16,027	—	25	60
Hiroshima	45,220	82,637	—	48	158
Yamaguchi	35,000	108,500	—	15	40
Tokushima	101,986	109,435	—	19	30
Kagawa	800	—	—	3	12
Ehime	77,963	103,742	27,650	22	53
Kochi	3,883	7,048	—	6	16
Fukuoka	11,039	3,240	—	7	8
Nagasaki	9,210	7,594	—	2	10
Kumamoto	5,210	6,531	874	8	21
Oita	166,125	301,907	—	16	55
Miyazaki	29,370	101,755	—	21	61
Kagoshima	4,845	6,086	272	9	34
Total Tons	2,884,000	3,750,000	962,000		

ENCLOSURE (C)

Table II(C)
PRODUCTION OF PINE ROOT OIL IN 1944

Name of Prefecture	Numbers of Dry-Distillation Units				Numbers of Workers	
	Working	Stopped	Repairing	Total	Producers of crude pine root oil	Refiners of pine root oil
Aomori	2	3	1	6	3	0
Iwate	13	1	1	15	10	1
Miyagi	31	10	5	46	20	1
Akita	9	3	1	13	8	1
Yamagata	20	22	6	48	40	0
Fukushima	15	18	5	38	30	1
Ibaragi	35	25	8	68	40	3
Tochigi	18	9	3	30	19	2
Gumma	7	2	1	10	5	
Saitama	8	0	0	8	6	2
Chiba	132	10	12	154	64	2
Tokyo	4	0	0	4	2	6
Kanagawa	7	6	1	14	1	1
Niigata	21	8	4	35	15	2
Toyama	4	5	1	10	5	
Ishikawa	20	7	3	30	20	1
Fukui	30	15	6	51	14	2
Yamanashi	29	18	6	53	32	5
Nagano	21	20	7	48	25	6
Gifu	20	2	2	24	16	4
Shizuoka	28	10	4	42	11	2
Aichi	39	8	5	52	12	2
Mie	7	3	1	11	6	
Shiga	20	10	4	34	20	1
Kyoto	18	45	11	74	17	3
Osaka	10	15	3	28	13	11
Hyogo	61	30	10	101	65	6
Nara	53	3	6	62	34	
Wakayama	10	20	5	35	9	
Tottori	40	50	14	104	28	4
Shimane	155	18	13	186	36	3
Okayama	128	9	14	151	10	2
Hiroshima	187	18	20	225	80	11
Yamaguchi	40	6	5	51	32	4
Tokushima	50	6	6	62	37	6
Kagawa	28	1	3	32	1	1
Ehime	61	40	10	111	36	7
Kochi	19	10	4	33	18	1
Fukuoka	18	15	5	38	18	3
Saga	0	0	0	0	1	
Nagasaki	14	4	2	20	10	1
Kumamoto	50	4	6	60	28	1
Oito	0	18	4	22	18	1
Miyazaki	40	13	7	60	23	
Kagoshima	11	17	5	23	9	
Okinawa	0	0	0	0	0	0
Total	1533	557	244	2330	947	110

ENCLOSURE (C)

Table III(C)
COST OF PINE ROOT OIL, NEW AND OLD

Products	Production price for 1 To			Selling price of regulation organs		
	Old	New	Per cent Increase	Old	New	Per cent Increase
Crude pine root oil	11.50	31.50	173	12.00	33.40	178
Total pine root oil and tar	10.00	25.90	159	10.50	27.45	161
Pine root tar	9.20	22.20	142	9.60	23.55	144
Rope tar	10.70	28.00	162	11.20	29.70	164

Note: 1 To = 18 liters

Table IV(C)
DRY DISTILLATION DETAILS

Time (o'clock)	Temperature (°C) Center of Retort R	L	Separator R	L	Cooler Inlet R	L	Cooler Water	Distillate from Tar-Separator Sum (kg)	Oil (cc)	Sum (lit)	Tar (cc)	Sum (lit)	Pyrolig. (cc)	S.G.	Sum (lit)	Distillate from Cooler Sum (kg)	Oil (cc)	S.G.	Sum (lit)	Tar (cc)	Sum (lit)	Pyrolig. (cc)	S.G.	Sum (lit)	Fuel R (kg)	L (kg)
0700																									10	10
0730																									10	10
0800																									10	10
0830	38	39	12	11																						
0900	55	58	8	9																						
0930	79	80	8	8																						
1000	90	84	85	93		88		8.4	2120	2.1			6300	1.012	6.3							1025		1.025		10
1030	93	85	100	98				7.7/16.1	1010	3.11			6700	1.010	13.0	1.5	130	0.9004	0.13			1370	1.014	2.395		
1100	96	96	98	93	65	89		4.4/20.5			130	0.13	4270		17.27	9/10.5	2850	0.8744	2.99	100	0.100	6040		8.435		
1130	97	99	95	95	140	95		3.0/23.5			70	0.2	2730	1.007	20.2	9.8/20.3	1600	0.8921	4.59	70	0.170	8130	1.015	16.565	10	
1200	105	93	96	93	70	90	14.6	2.8/26.3					2800		23.0	15.5/35.8	3050	0.8965	7.64			13.450		30.015		10
1230	117	114	95	95	74	98	16.5	3.2/29.5			380	0.58	2800	1.012	25.82	18.8/55.6	3480	0.9399	11.12			15.320	1.008	45.335		
1300	143	161	97	97	77	106	17.0	5.4/34.9			3000	3.58	2400		28.22	23.2/78.8	8130	0.9832	19.25			15.070		50.405	10	
1330	160	215	103	90	83	122	20.5	12.2/47.1			12200	15.78				26.0/104.8	5300	0.9691	24.55			20.700	1.017	71.105		
1400	185	250	101	94	72	122	25.4	9.2/56.3			9200	24.98				21.5/126.3	5050	1.0112	29.6			16.450		87.555		
1430	205	257	110	93	72	84	22.5	8.8/65.1			8800	33.78				13.5/139.8	3600	0.9832	33.2			9.900	1.010	97.455		
1500	231	269	132	93	88	69	24.0	9.2/74.3			9200	42.98				12.5/152.3	3450	1.0032	36.65			9.050		106.505	10	
1530	282	280	151	82	94	58	23.0	5.2/79.5			5200	48.18				14.0/166.3	3400	1.0625	40.05			10.600	1.032	117.105		
1600	313	270	152	71	75	46	22.5	3.4/82.9			3400	51.58				12.0/178.3	4800	1.0435	44.85			7.200		124.305		
1630	310		100	54	46		20.0	1.0/83.9			1000	52.58				1.5/179.8	350		45.20			1.150		125.455		
1700	300		70		60		17.0																			
1730																									60	50

Notes:

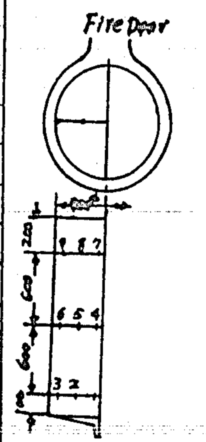
0.830: First Drop of Pyroligneous Liq. from Tar Separator
0.940: First Drop of Tar from Tar-Separator
1025: First Drop of Oil from Cooler
1220: Non-Condensed Gas is beginning to burn at Fire Door

Feed: Pine-Root (water-content .... 37%)
Charged - Right .... 253 kg
Left .... 249 kg
Fuel (Wood Charcoal) - Right .... 49.5 kg
Left .... 46.5 kg

ENCLOSURE (C)

Table V(C)
TEMPERATURE DISTRIBUTION IN CARBONIZATION RETORT
FEED: PINE-STEM

Time (o'clock)	Temperature in Retort (°C)								
	1	2	3	4	5	6	7	8	9
0900	29	27	36	33	45	53	43	44	56
0930	37	34	49	40	56	80	55	54	74
1000	51	45	60	53	70	93	62	62	85
1030	57	53	70	62	87	106	65	71	96
1100	64	62	85	68	90	117	93	75	103
1130	70	68	90	73	92	115	80	82	103
1200	77	74	99	82	115	140	85	89	106
1230	64	81	105	84	118	128	88	93	100
1300	87	84	113	88	125	144	90	96	102
1330	93	88	132	90	128	165	97	99	115
1400	92	85	135	93	140	203	102	102	140
1430	92	85	138	93	145	228	108	108	150
1500	92	87	150	96	156	238	113	120	158
1530	98	85	146	100	170	257	117	124	167
1600	100	88	150	101	173	277	116	131	180
1630	100	88	147	100	160	257	127	136	180
1700	94	86	163	105	180	287	83	102	201
1730	97	116	150	110	180	288	123	165	212
1800	103	90	155	115	187	283	152	180	213
1830	97	92	146	117	188	283	153	185	219
1900	102	95	175	125	202	303	156	218	234
1930	102	98	177	134	230	326	165	220	243
2000	107	102	158	144	241	331	168	227	250
2030	125	104	152	162	245	303	183	226	238
2100	127	107	143	175	247	296	173	213	230
2130	140	120	156	192	262	322	202	212	258



MEASURING POSITION

ENCLOSURE (C)

Table VI(C)
PROPERTIES OF PINE ROOT OIL

		Crude pine root oil	Pine root tar	Total pine root oil and tar
Specific gravity (d_4^{20})		0.964	1.070	0.990
Distillation (°C)	150	3.4 (0.6)	4.0(4.5)*	3.7(0.8)*
	150-200	50.5	5.8(1.2)*	31.0
	200-250	11.2	6.0	12.1
	250-300	11.2	9	7.1
	300-330	10.3	55.5	25.5
	Residue (in 100cc)	19.1 gm	15.2 gm	19.0 gm

* Numbers in bracket show water content.

Table VII(C)
RESULTS OF WASHING AND CORROSION EXPERIMENT

	Degree of Washing (1)	Acid Equivalence(2) N-NaOH cc	Corrosion with Mild Steel Pieces (3), Weight Loss (gm)		Volume Decreased by Washing
			Room Temperature	140°C	
Total pine root oil and tar	no washing	10.25	0.0584	0.0510	—
	3% NaCl-solution	4.45	0.0159	0.0221	2
	3% NaCl-solution 1% $Ca(OH)_2$-solution	2.10	0.0106	0.0063	5
Crude pine root oil	no washing	7.70	0.0477	0.0529	—
	water (once)	3.55	0.0272	—	2.5
	water (twice)	2.50	—	0.0108	4.0
	1% $Ca(OH)_2$-solution	2.10	0.0045	0.0049	4.0

Notes:

1. The oil is washed at 80°C with an equal amount of liquid.

2. Acid equivalence indicates the amount of 1N NaOH solution neutralizing 50cc of the fraction below 250°C.

3. Corrosion test with mild steel pieces are carried out with test-pieces weighing 30-34 grams.

ENCLOSURE (C)

Table VIII(C)
EXPERIMENTS OF PINE TRUNK DRY DISTILLATION

No. of Experiment	Weight of Materials (kg)	Water Content (1) (%)	Yield: Tar (1)	Yield: Crude Oil (1)	Yield: Total (1)	Yield to Weight of Material (%)	Fuel: Weight Consumed: Fire-wood (kg)	Fuel: Weight Consumed: Char-coal (kg)	Fuel: Weight Consumed: Total (kg)	Fuel: Consumption Ratio to wt. of Material	Operation Time (hrs)
1	280	22.16	26.68	4.39	25.07	4.6	80	43	123	1/2.3	12.5
2	280	35.2	-	-	-	-	80	43	123	1/2.3	12.5
3	280	26.8	13.96	4.08	18.04	3.2	90	43	133	1/2.1	12.5
4	280	22.3	-	-	-	-	70	43	113	1/2.5	10.2
5	300	29.1	21.44	3.74	25.18	4.2	110	20	130	1/2.3	11.6
6	300	30.0	-	-	-	-	135	20	155	1/2.0	11.7
7	170	5	large amount of tar and crude oil leaked out		20.4	6.0	60	-	60	1/3.0	6.0
8	170	5	-	-	-	-	60	-	60	1/3.0	6.0
9	345	45	23.21	1.224	24.44	3.5	85	55	140	1/2.5	12.0
10	345*	34.5	-	-	-	-	65	45	110	1/3.1	11.0
11	288	21	27.01	0.24	27.25	4.7	40	55	95	1/3.0	10.0
	288*	21	-	-	-	-	20	55	75	1/3.8	10.0

Note: (1) Water content = $\frac{\text{(original weight--wt. after drying)}}{\text{original wt.}} \times 100$

(2) * Mark shows cases using central basket in the retort.

(3) Average age of "Kuromatsu" is about 60 years.

ENCLOSURE (C)

Table IX(C)
DRY DISTILLATION OF JAPANESE CYPRESS

Month	Number of Retorts	Materials (kg)	Products			
			Crude Oil (l)	Pyroligneous Liquor (l)	Tar (l)	Charcoal (kg)
7	15	4137	468	1304	—	100
8	39	11607	988	4259	—	2688
9	34	10100	739	4208	51.7	2268
10	25	6913	791	3400	38.1	1652
11	22	6380	587	2865	37.5	1487
12	19	5440	523	2442	33.0	1294
Sum	154	44579	4090	18514	160.3	9498

Table X(C)
RESULTS OF EXTRACTION

	Tree	Yield (%)
Leaves	Cyptomeria Pine Japanese cypress	15.5 10.9 11.6
Twigs	Cyptomeria Pine Japanese cypress	3.55 6.11 2.88

ENCLOSURE (C)

Table XI(C)
CATALYTIC DRY DISTILLATION OF VARIOUS TREES

Trees	Crude Oil			Distilled Liquid		
	Total Volume cc/100 gm Original Wood	Distilled Oil % to Original Wood	~200°C Light Oil, % to Original Oil	Total Volume cc/100 gm Original Wood	Contents of Acetone & Methanol % to Original Wood	Charcoal gm/100 gm
Sawara (Japanese-cypress	6.25	71.8	25.8	41.2	3.25	28.5
Tsuga (Japan hemlock-spruce)*	4.58	69.8	29.4	44.3	2.35	24.2
Asunaro (Hatchet leaved arborvitae)*	4.46	64.4	24.0	49.4	1.77	24.6
Himekomatsu (Pinus parviflora)*	5.20	75.5	25.1	48.1	1.90	24.8
Mizuna (Brassica-Japonica)*	4.50	38.5	21.8	50.3	1.70	21.5
Buna (Fagus Sieboldi)*	3.92	51.2	22.4	54.0	2.83	20.6
Nara (Quercus glandulifera)*	3.81	71.1	40.0	52.0	4.23	23.5
Nara (Quercus glandulifera)**	3.5	39.2	39.2	44.3	4.4	25.0
Nire (Elm-tree)**	4.7	27.3	27.3	45.1	7.3	23.9
Makaba (Birch-tree)**	4.5	37.5	30.0	42.5	6.5	23.8
Katsura (Cercidiphyllum Japonicum)**	3.61	43.0	43.0	41.1	6.4	25.8
Buna (Fagus Sieboldi)**	5.41	43.2	27.0	-	-	-

* Kiso
** Nikko

ENCLOSURE (C)

Table XII(C)
DRY DISTILLATION OF BIRCH BARK

Product	Yield (%)	Per 1 ton of air dried bark (kg)
Tar	49.5	495
Water solution	17.5	175.7
Gas	13.4	100 m^3
Charcoals	20.7	207.2

(See page 168 for Table XIII(C).)

Table XIV(C)
DEMAND AND SUPPLY OF PINE RESIN

	Amount Produced (ton)	Amount Demanded (ton)	Note
Japan	1,000	28,000	Chiefly imported from U.S.A.
Manchukuo	-	500	Chiefly imported from U.S.A.
China	500	3,300	Chiefly imported from U.S.A.
French China	1,300	400	Exported to Japan
Sumatra	9,700	-	—
Java	-	13,000	Imported from Sumatra

ENCLOSURE (C)

Table XIII(C)

PROPERTIES OF NEUTRAL DISTILLATE, FROM BIRCH BARK DRY DISTILLATION

Fraction No.	Temperature (°C)	Specific Gravity (d_4^{20})	Refractive Index (20°C)	Viscosity (30°)		Iodine Value	Distillate Ratio	Note
				Specific Vis. 7/9	Redwood (Second)			
1	~100	0.744	1.424	0.861	-	116.3	1.62	Light yellow
2	100 ~ 150	0.788	1.442	0.947	-	105.5	3.10	Light yellow
3	150 ~ 175	0.822	1.458	1.233	-	102.9	3.12	Light yellow-green
4	175 ~ 200	0.850	1.470	1.639	-	101.9	3.69	Yellowish green
5	200 ~ 225	0.870	1.481	2.158	-	97.0	4.01	Deep green
6	225 ~ 250	0.884	1.490	2.872	-	91.5	5.52	Deep green
7	250 ~ 275	0.901	1.497	4.868	35.4	85.9	13.45	Light yellowish black
8	275 ~ 300	0.912	1.504	8.947	43.8	85.4	13.11	Light yellowish black
9	300 ~ 325	0.930	1.515	16.692	62.1	77.7	12.49	Fluorescence begins
10	325 ~ 350	0.956	1.529	54.962	180.4	77.4	12.33	Fluorescence
11	350 ~ 375	0.972	1.541	92.669	300.1	75.8	17.81	Deep greenish-brown
	Residue						2.44	
	Loss						7.31	

ENCLOSURE (C)

Table XV(C)

DRY-DISTILLATION OF PINE-RESIN

Experi-ment No.	Wt. of Raw Materials (gm)		Distilled Amount (cc)	Yield Ratio % per weight of Resin	Oil Distilled			
	Resin	Clay			Appearance	Sp. Gr.	Acid-Value	Iodine Value
1	50	25	35	63	Slightly green	0.9024	1.8	25.9
2	50	50	32	57	Transparent Blue-White	0.8898	0.9	24.2
3	50	100	25	44	Transparent Blue-White	0.8751	-	-
4	200	200	127	57	Transparent Blue-White	0.9009	2.3	24.3
5	200	300	96.5	42	Transparent Blue-White	0.8739	0.6	19.0

Method	Raw Material		Oil (1)			Acetone Methanol (2) (1)	Sub-stitute Gasoline (1)+(2) (1)
	Kind	Amount	Gasoline (1)	Light Oil Heavy Oil	Total		
Catalytic cracking	Na-pulp waste solution + wood waste (kg)	1,000	80-220°C 10.63	200-300°C 22.13	32.76	2.74	19.37
Dry-distillation	Boiled water (kg) 1 kg wood piece	1,030	378	5.62	9.40	3.13	6.91

Note: Amounts were assumed from experimental results. Raw material was a concentrated waste pulp solution mixed with 10% waste wood.

ENCLOSURE (C)

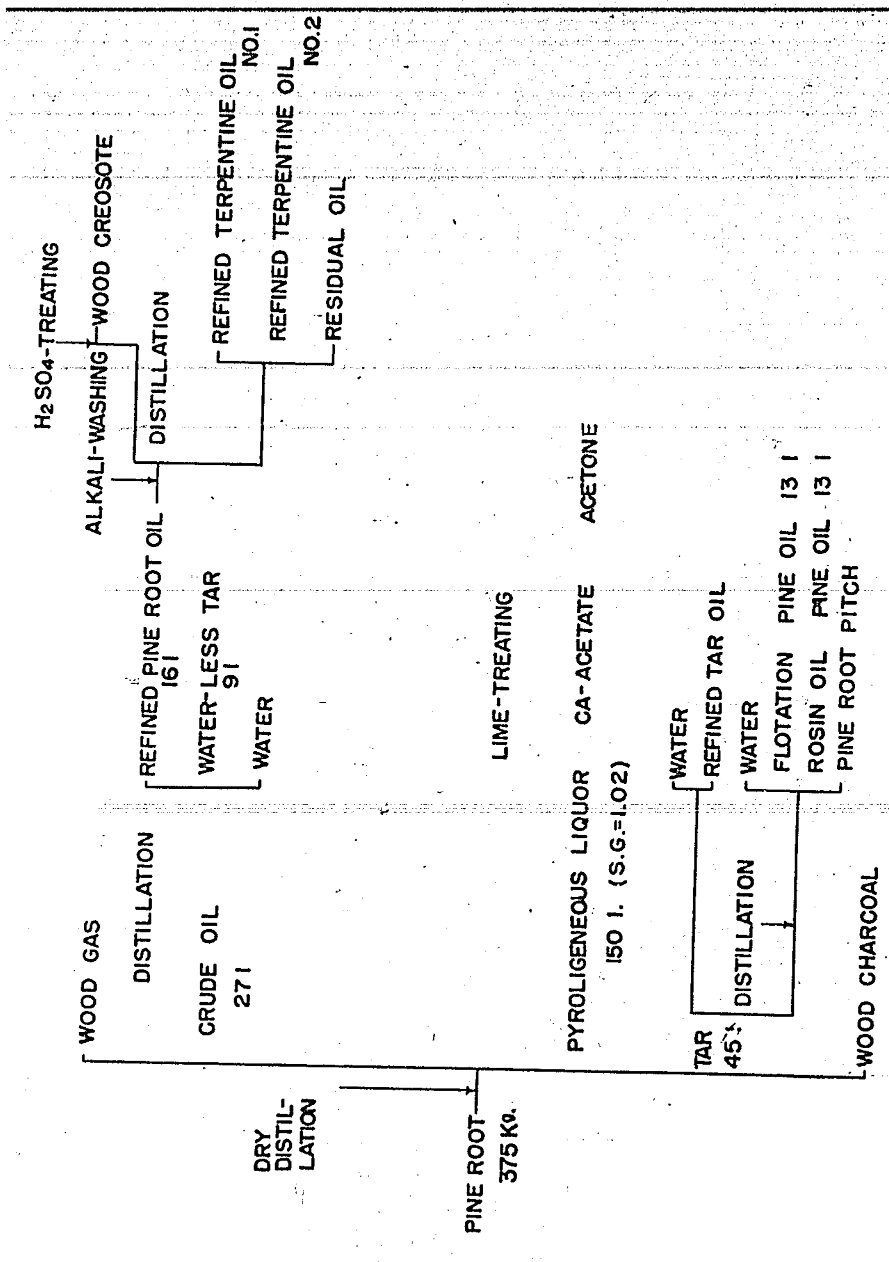


Figure 1(C)
FLOW SHEET OF REFINING PINE ROOT OIL
Vertical Retort

ENCLOSURE (C)

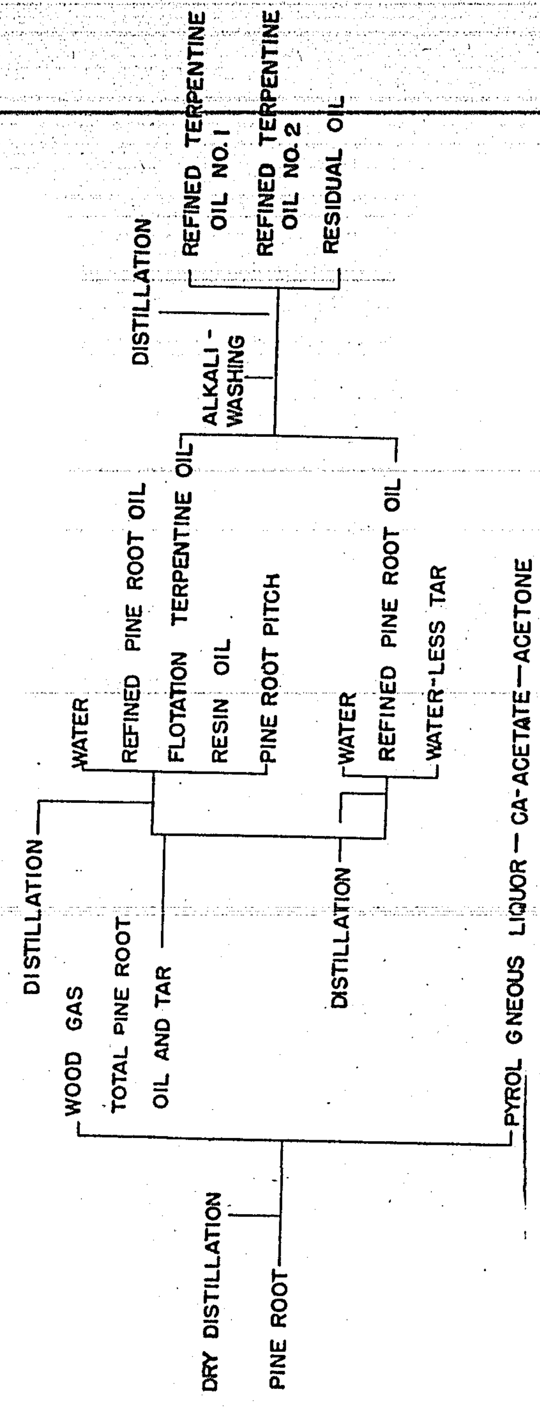


Figure 2(C)
FLOW SHEET OF REFINING PINE ROOT OIL
Horizontal Retort

ENCLOSURE (C)

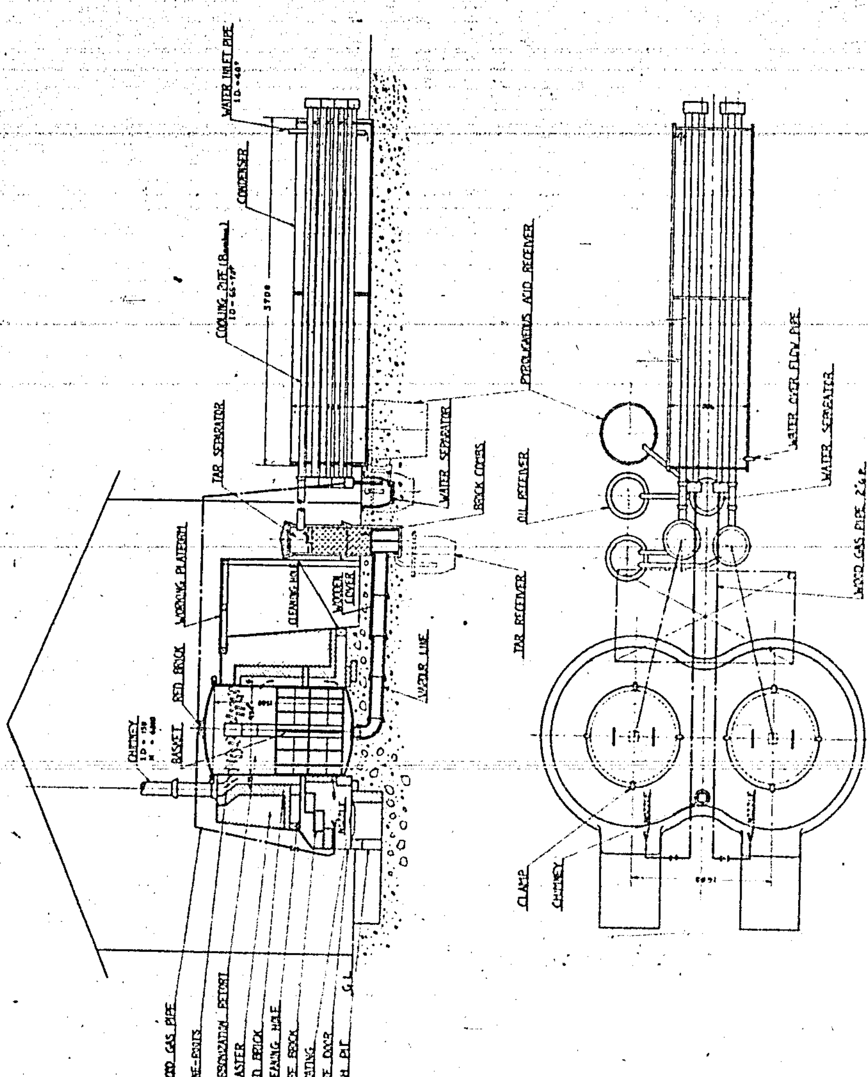


Figure 3(C)

GENERAL ARRANGEMENT OF CARBONIZATION APPARATUS OF PINE-ROOT

Daily Capacity 750kg/1 set

ENCLOSURE (C)

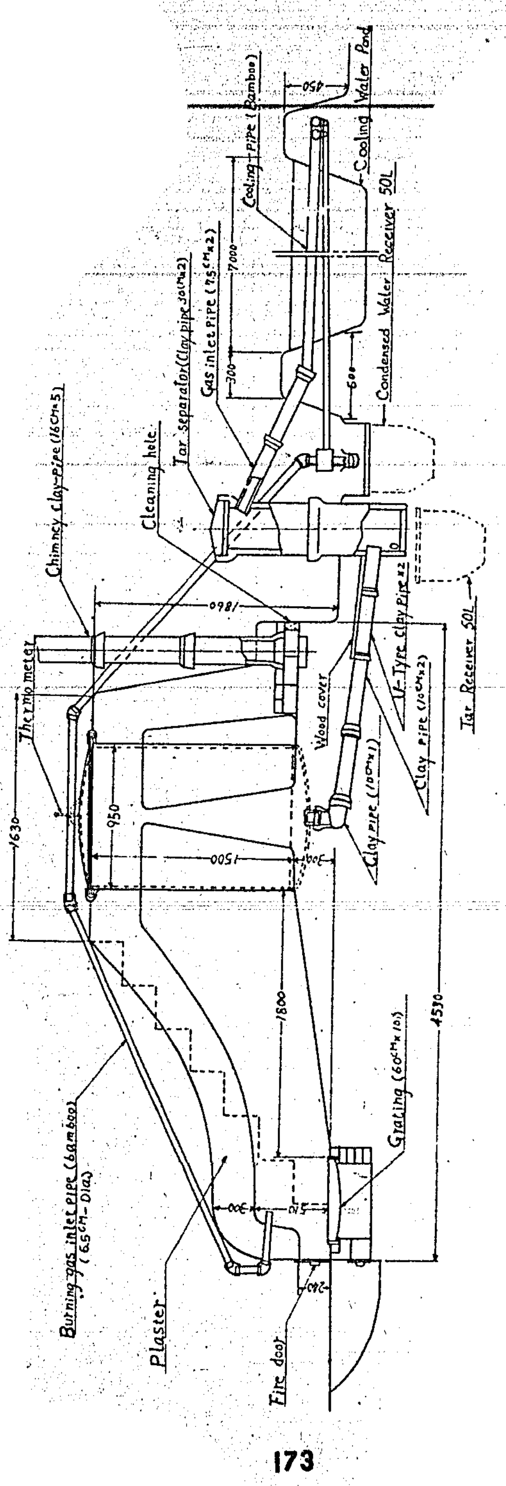


Figure 4(C)

SIDE-VIEW OF YAMAMOTO-TYPE CARBONIZATION APPARATUS OF PINE-ROOT

Daily Capacity 375kg/1 set

ENCLOSURE (C)

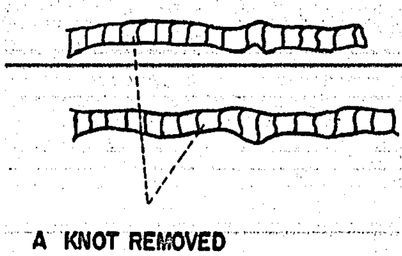


Figure 5(C)
INCLINED BAMBOO COOLING TUBE

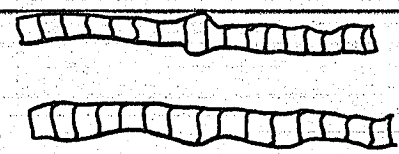


Figure 6(C)
HORIZONTAL BAMBOO COOLING TUBE

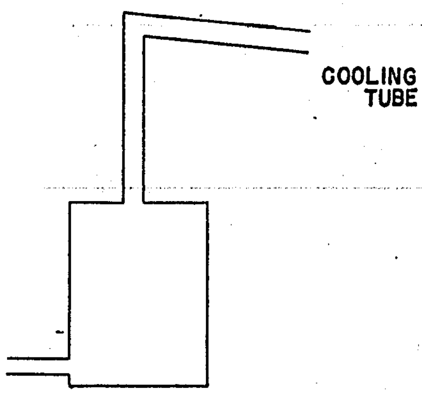


Figure 7(C)
VERTICAL APPARATUS

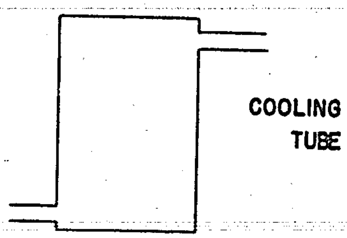


Figure 8(C)
HORIZONTAL APPARATUS

ENCLOSURE (C)

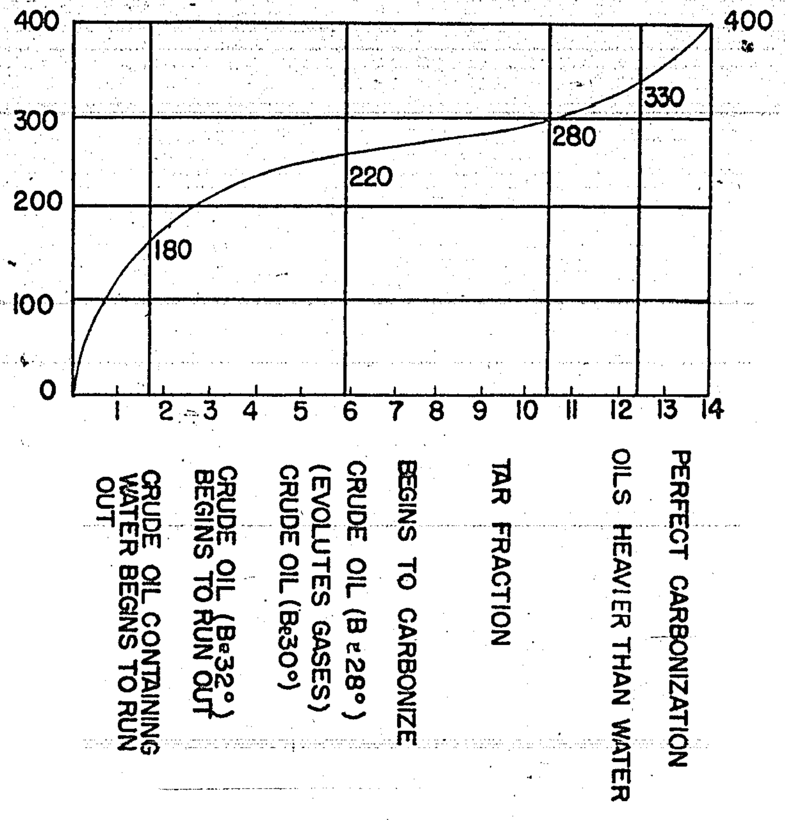


Figure 9(C)
PROGRESS OF DISTILLATION

ENCLOSURE (C)

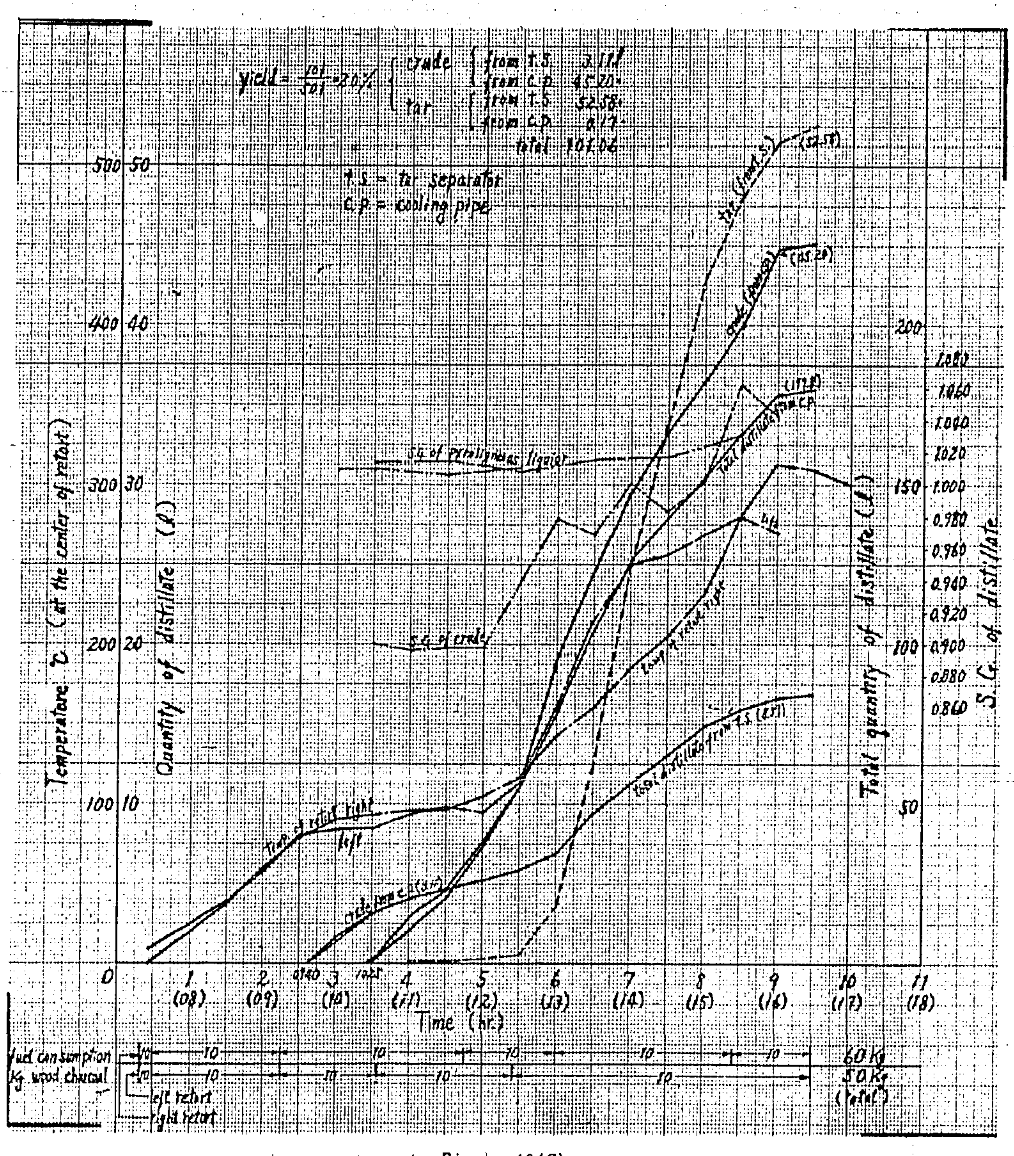


Figure 10(C)

CURVES OF THE TEMPERATURE OF RETORT,

FEED OF DISTILLATE AND THE SPECIFIC GRAVITY OF DISTILLATE

The weight of packed pine root--left 248kg., right 253kg.

ENCLOSURE (C)

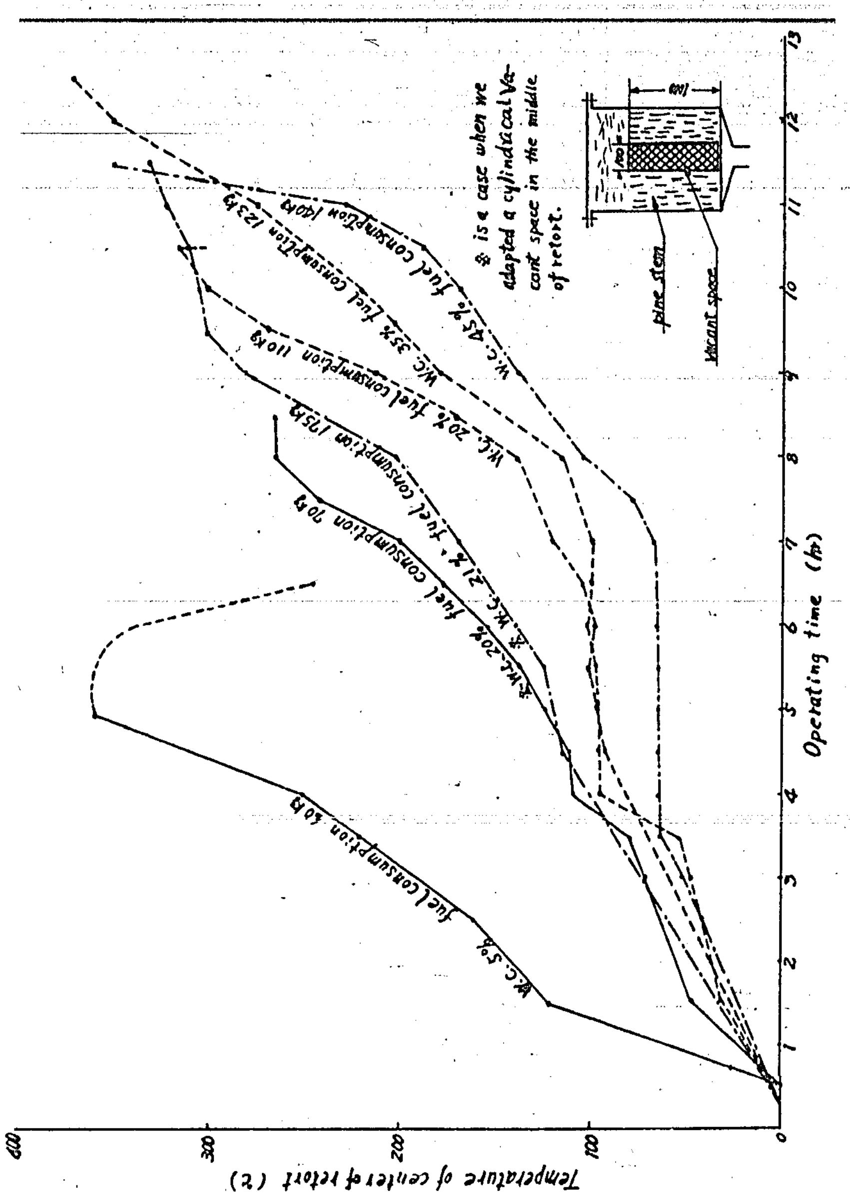


Figure 11(C)

RELATION BETWEEN THE TEMPERATURE OF THE CENTER OF RETORT AND THE WATER CONTENT OF PACKED PINE STEM

A Type Apparatus

ENCLOSURE (C)

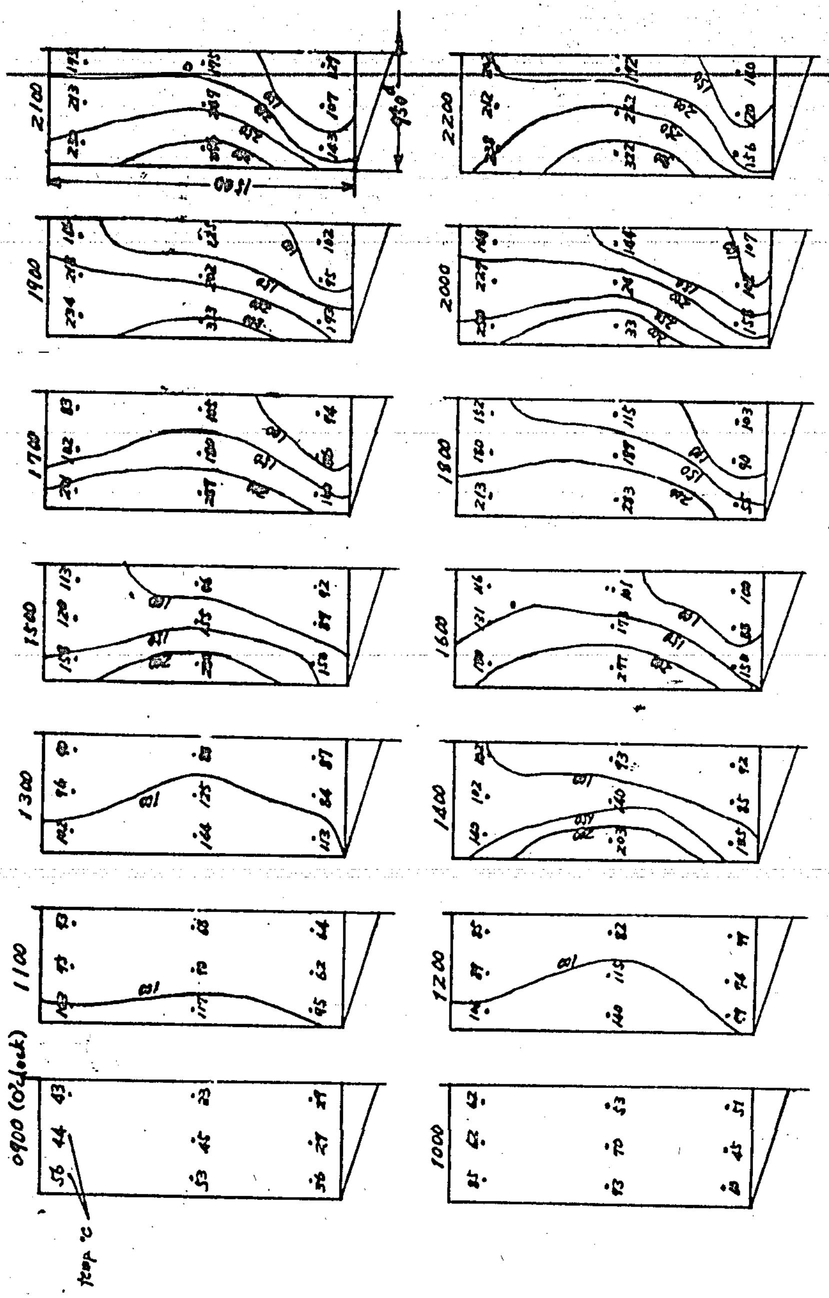


Figure 12(C)
THE CHANGE OF THE TEMPERATURE DISTRIBUTION IN THE RETORT (USING THE PINE STEM)
(A Type Retort)

ENCLOSURE (C)

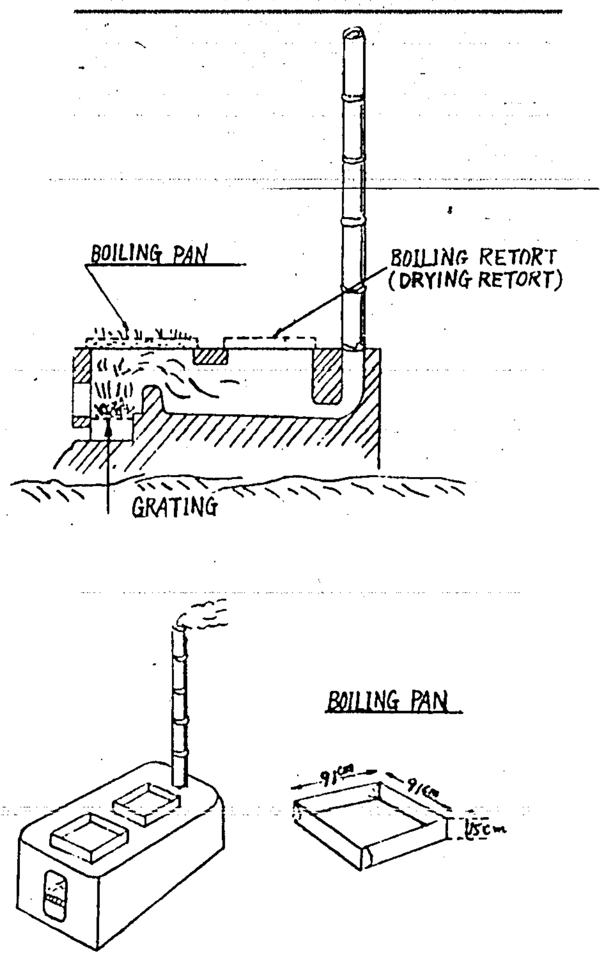


Figure 13(C)
BOILING PAN OF PYROLIGNEOUS LIQUOR

ENCLOSURE (C)

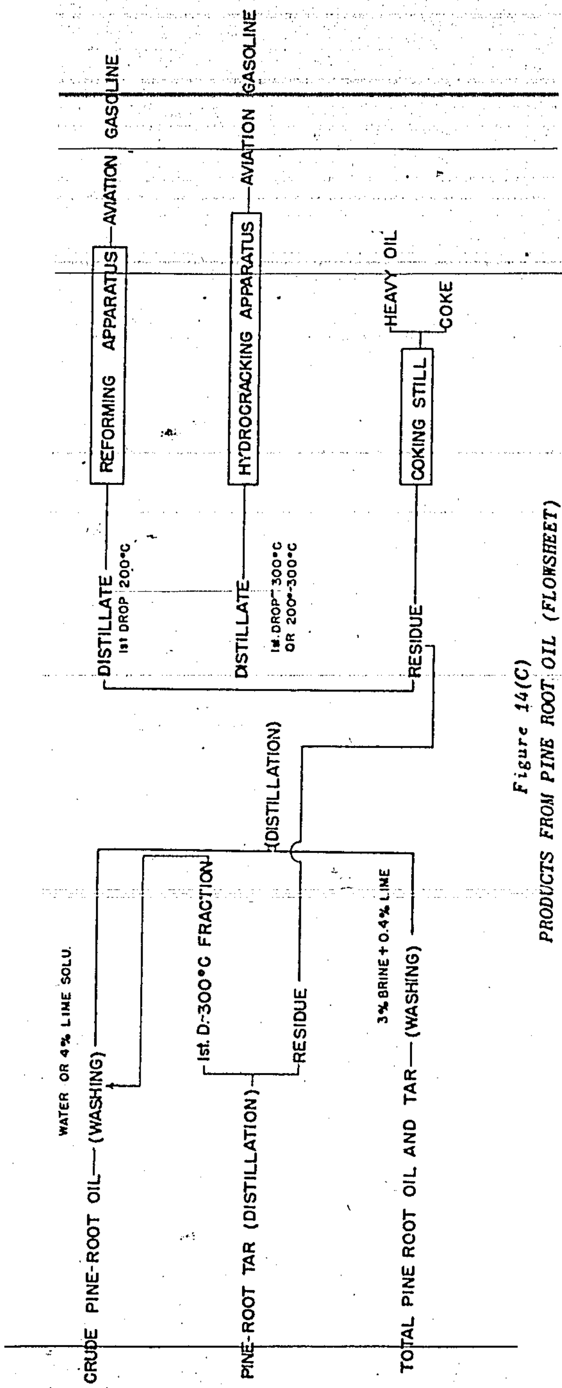


Figure 14(C)
PRODUCTS FROM PINE ROOT OIL (FLOWSHEET)

ENCLOSURE (C)

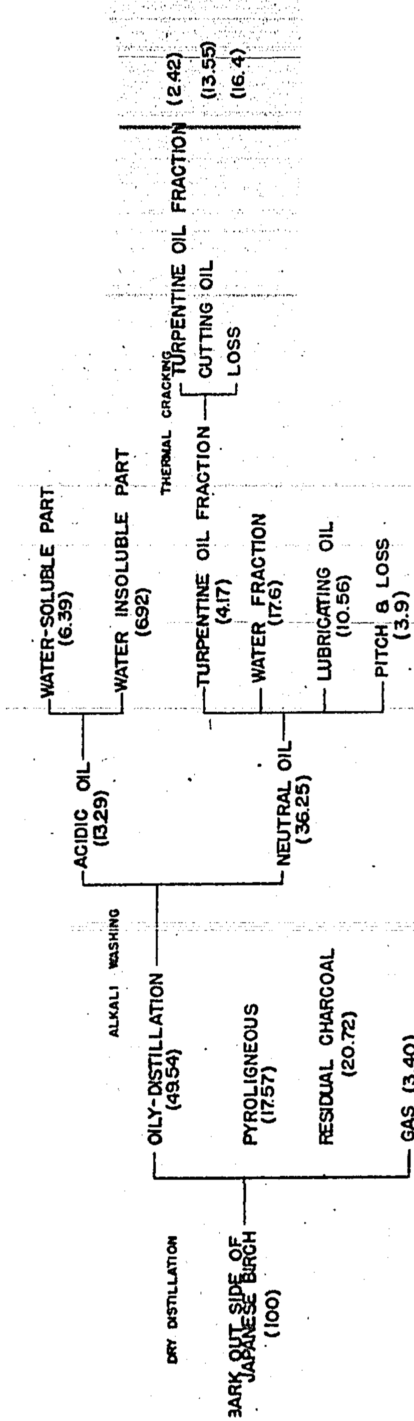


Figure 15(C)
PRODUCTS FROM JAPANESE BIRCH (FLOWSHEET)