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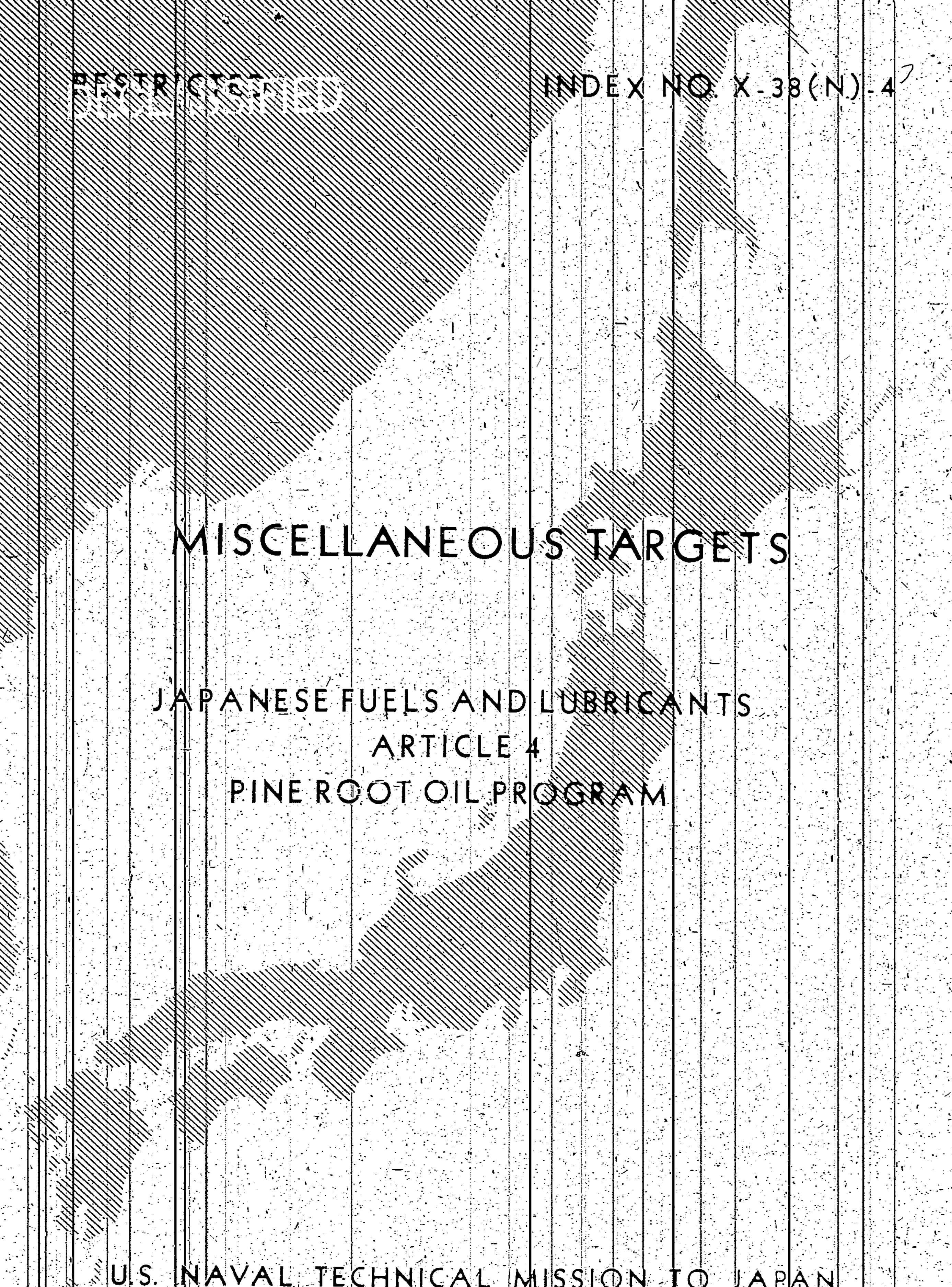

MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS
ARTICLE 4
PINE ROOT OIL PROGRAM

U.S. NAVAL TECHNICAL MISSION TO JAPAN

U. S. NAVAL TECHNICAL MISSION TO JAPAN
CARE OF FLEET POST OFFICE
SAN FRANCISCO, CALIFORNIA

6 February 1946

RESTRICTED

From: Chief, Naval Technical Mission to Japan.
To : Chief of Naval Operations.

Subject: Target Report - Japanese Fuels and Lubricants, Article 4 - Pine Root Oil Program.

Reference: (a)"Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Subject report, covering the pine root oil program in Japan outlined by Targets X-09, X-10, and X-38(N) of Fascicle X-1 of reference (a), is submitted herewith.

2. The investigation of the target and the target report were accomplished by Comdr. G. L. Neely, USNR, Lt. Comdr. C. S. Goddin, USNR, and Lieut. W. H. Millet, USNR, assisted by Ens. E. R. Dalbey, USNR, as interpreter and translator.

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Captain, USN

JAPANESE FUELS AND LUBRICANTS
ARTICLE 4
PINE ROOT OIL PROGRAM

"INTELLIGENCE TARGETS JAPAN" (DNI) OF 4 SEPT. 1945
FASCICLE X-1, TARGETS X-09, X-10, AND X-38(N)

FEBRUARY 1946

U.S. NAVAL TECHNICAL MISSION TO JAPAN

SUMMARY

MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 4
PINE ROOT OIL PROGRAM

The Japanese program for obtaining aviation gasoline and other liquid fuels from the dry distillation product of pine roots has been investigated. This program called for the erection of 36,000 small scale distillation units throughout Japan having an annual capacity of 2,500,000 barrels of pine root crude oil on a one to two year basis. By subsequent catalytic cracking or hydrocracking of this crude oil, it was planned to produce annually some 400,000 barrels per year of an aviation gasoline having an octane number of 90-94 with 0.15 per cent volume of lead. Full scale tests showed the performance of this fuel to be comparable to that of conventional aviation gasolines. An interesting technical development of this program was the successful catalytic conversion on a commercial scale of terpenes to aromatics. This source of fuel is not economically feasible in peace time, and it can only be considered as an emergency measure necessitated by the acute scarcity of conventional hydrocarbon-type fuels in the closing year of the war. However, the program is of significance in that it demonstrates the technical resourcefulness of the Japanese in the face of impending disaster.

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The Report

LIST OF ENCLOSURES

REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA, Kanagawa Prefecture
Third Naval Fuel Depot, TOKUYAMA
First Naval Technical Depot, YOKOSUKA
Army Fuel Research Institute, FUCHU
Imperial Fuel Research Institute, KAWAGUCHI, Saitama Prefecture
Miike Synthetic Oil Company, OMUTA, Kyushu
Toyoda Factory of Totsuka Agricultural Society, TOTSUKA, Kanagawa Prefecture
Kyushu Imperial University, FUKUOKA, Kyushu
Mitsubishi Resin-Oil Factory, SHIMABARA, Nagasaki Prefecture, Kyushu

Japanese Personnel Interviewed:

S. KOMATSU, Ph. D., Civilian Advisor to Department of Fuel Research, First Naval Fuel Depot, (formerly Professor of Biochemistry at Kyoto Imperial University, foremost and very capable chemist of First Naval Fuel Depot).
H. FUJIMOTO, Ph. D., Engineering Commander, IJN, Head of Cracking, Dry Distillation, and Pine Root Oil Sections First Naval Fuel Depot, (research engineer of high capability).
S. SANKA, Engineering Lieutenant Commander, IJN, Head of Process Engineering Section of the First Naval Fuel Depot, (design engineer of high capability).

Research Assistants of the First Naval Fuel Depot, whose names are included in individual Japanese reports.

T. KONDO, Captain, IJN, Head of Aviation Gasoline Testing, First Naval Technical Depot, YOKOSUKA.
I. WATANABE, Engineering Rear Admiral, Japanese Navy, Superintendent of Third Naval Fuel Depot, TOKUYAMA.
N. TAKEI, Chief Chemical Engineer of Miike Synthetic Oil Company, OMUTA, Kyushu.
ISHIGARA, Business Manager of Mitsubishi Resin-Oil Factory, SHIMABARA, Kyushu.
KIROSHIMA, Ph. D., Professor of Fuel Chemistry, Kyushu Imperial University, FUKUOKA, Kyushu.

Referenced Japanese Reports

Technical Notes on Research Work, Army Fuel Research Institute, FUCHU.

INTRODUCTION

The manufacture of aviation gasoline from the product of the dry distillation of pine roots constitutes the principal and one of the most interesting emergency fuel measures adopted by the Japanese during the final period of the war. This report summarizes a mass of detailed technical information which has been obtained by the Petroleum Section of the U. S. Naval Technical Mission of Japan relative to pertinent research activity and the application of this research to the production of pine root gasoline. The history of the program is discussed, and the various methods of refining the oil are described. The properties of the fuel produced from pine root oil as well as the engine performance characteristics of this fuel are reported. Japanese research pertaining to the utilization of vegetable products of similar nature has also been investigated.

Although both the Japanese Army and Navy were engaged independently in research program on pine root oil, the emphasis of this report is on the Navy's activities since the Naval research was more complete and further advanced than that of the Army. Detailed research reports of the pine root oil research projects investigated at the First Naval Fuel Depot have been prepared in English by the Japanese technical personnel of the Depot and are included in this report as Enclosures (B)1 to (B)11, inclusive. Summaries of this research and the chemistry of pine root oil have been prepared in English by Chemical Engineering Commander H. FUJIMOTO, IJN, and Dr. S. KOMATSU, respectively. These summaries are submitted herewith as Enclosure (A). Supplementary information has been obtained by visits to various research laboratories, refineries, and rural distilling installations throughout Japan.

Since all of the research files of the First Naval Fuel Depot were burned in August 1945 by order of the Director of the Depot, it was necessary to recall the Japanese personnel to reconstruct this information from laboratory notebooks, laboratory apparatus, and pilot plant equipment. The preparation of these reports and drawings continued for a period of nearly three months, during which time each Japanese author was frequently interrogated and was assisted by the Petroleum Section of the U. S. Naval Technical Mission to Japan in the organization and translation of his reports. The material which is submitted as Enclosures (A) and (B) constitutes an integral part of this report, and although it may include minor errors in construction introduced in the translation by the Japanese authors, it does serve as an accurate indication of the quality and extent of Japanese research relative to the production of aviation gasoline from pine root oil.

THE REPORT

Part I
HISTORY OF PINE ROOT OIL PROGRAM

Prior to 1944 pine root oils were utilized for a variety of applications including their use as solvents, flotation oils, and as raw material for the synthesis of drugs and special chemicals. Up to this time they had never had seriously considered as a source of fuel. The annual production of pine root oil in Japan was essentially the same in 1944 as in 1941, - approximately 6,000 kiloliters. However, by the end of 1944, the Japanese Army and Navy as well as the Japanese civil government were devoting frantic efforts towards the proposed utilization of this material for the synthesis of high-grade aviation gasoline. More than one hundred million yen were allocated for this purpose by the Japanese government.

Early in 1944 Army laboratories approached the problem by directing their research towards the utilization of existing equipment for the refining of the crude pine root oil. However, as the refineries were increasingly damaged by bombings, it became necessary to concentrate on the fabrication of small scale equipment which could be easily constructed.

By August 1944, the Navy's research program was in full swing. Laboratory studies on the characteristics of pine root distillates were being made, and designs of simplified distillation retorts were being selected. In December 1944 a plan was proposed in which prefectural governors were to take charge of pine root oil production in their particular prefecture. Pine root stumps were to be excavated by civilian workers or home service troops and then crude distilled by the farmers. The Army and Navy were each assigned districts in which they were to provide the equipment and be largely responsible for treating the crude oil.

Several treating methods were studied and those finally selected were chosen more for ease of construction and simplicity of design than for the quality of product obtained. It was planned to erect 36,000 retorts throughout Japan. The retorts would be of standard design and would produce 360,000 kiloliters per year of pine root oil. By June and July of 1945 this production was nearly realized.

In connection with this plan the Navy published a pamphlet entitled "Pine Root Oils" which presented a complete picture of the industry and the processes which were to be applied. A Japanese translation of this interesting pamphlet was prepared for inclusion in this report and is submitted as Enclosure (C).

During 1945 pilot plant tests on hydrocracking of pine root oils were being conducted, and the construction of twenty-one small scale catalytic cracking plants was planned. At the end of the war, construction had been started on a group of simplified catalytic reforming plants, although these units never were completed.

Part II
REFINING STUDIES

The refining of pine root gasoline from pine roots takes place in several successive or alternate steps. Each of the steps is described in detail in Enclosures (A), (B), and (C). There follows a brief discussion of each of these refining procedures.

A. DRY DISTILLATION AND FRACTIONATION

A Kitagawa vertical-type retort was selected as standard for the dry distillation. The yield of pine root oil varied from 10% to 25% of the weight of pine roots charged depending on the species of pine and the age of the roots. The retort selected could treat 350 kilograms of pine roots daily and the annual production of pine root crude would amount to approximately 10 kiloliters. Details of design are shown in Enclosure (B)1, and a complete description of the raw materials, apparatus, and procedures for dry distillation is presented in Enclosure (C).

Small scale batch-type stills were designed for the fractionation of the total pine root oil (Enclosure (B)4). The product was separated as follows:

1. Fraction boiling below 185°C. (Turpentine No.1)
2. Fraction boiling from 185°C-300°C. (Turpentine No.2)
3. Residual Oil. (Subjected to further dry distillation to yield bunker fuel.)

The chemical constituents of each of these fractions are discussed in Part II of Enclosure (A) and in Enclosure (C).

A typical distillation unit, slightly different in design than that proposed by the Navy, was visited by the U. S. Naval Technical Mission to Japan in October 1945. A report on this plant, located in SHIMABARA, Kyushu, is submitted herewith as Enclosure (D). A Navy-type distillation unit in TOTSUKA was also visited. Pictures of this unit are included as Figure 6 and 7 of Enclosure (B)1.

B. CONTACT DISTILLATION

One of the procedures studied by the Army Fuel Research Institute and other laboratories under the jurisdiction of the Army Fuel Bureau, such as that of the Miike Synthetic Oil Company, OMUTA, was the so-called contact distillation method, in which a slurry of pine root crude oil and Japanese acid clay was subjected to distillation followed by subsequent rectification of the distillate. The fuel obtained was high in unsaturates and of inferior grade. No extensive application of this method was applied.

C. CATALYTIC REFORMING

The simple catalytic reforming of the pine root oil fraction boiling below 185°C was the treatment which was studied in detail at the First Naval Fuel Depot. Research on this procedure and design data for the catalytic reforming units are outlined in Enclosures (B)3 and (B)4. The reforming was effected by means of Japanese acid clay at a temperature of 350°C and atmospheric pressure. The product was too low in volatility to be of direct use as a fuel but most of the unsaturates were transformed by this treatment. The gasoline was obtained in a yield of 12% by volume of the original total pine root oil, and it was planned to blend this product with alcohol for use as an aviation fuel.

The conversion of cyclic unsaturates of the mono-terpene type to aromatics and naphthenes was effected by this treatment. A discussion of this molecular rearrangement is presented by Dr. KOMATSU in Part II of Enclosure (A). It is Dr. KOMATSU'S personal opinion that the rearrangement in the presence of acid clay is catalyzed by the presence of traces of iron abietate, although no experimental data were presented to substantiate this hypothesis.

D. CATALYTIC CRACKING

Catalytic cracking of the two pine root oil fractions was investigated at the First Naval Fuel Depot. Both a U. O. P. catalyst, prepared by the Nippon Oil

Company, and Japanese acid clay catalysts were studied. It was decided to use this process with a clay catalyst for the pine oil fraction boiling from 185°C to 300°C. An aromatic base gasoline, having an octane number of 90-92 with 0.15% added lead, was obtained in 6% yield by volume of the original total pine root oil.

Pilot plant tests on this process are discussed in Enclosure (B)5 and design details of a simplified catalytic cracking unit are shown in Enclosure (B)6. It was planned to construct twenty-one of these catalytic cracking plants, each treating from 10-30 kiloliters per day, at centrally located refineries. Two large catalytic cracking plants at the Second Naval Fuel Depot, YOKKAICHI, having a 4,000 barrel per day capacity, were also to be utilized.

E. HYDROCRACKING

Enclosure (B)7 describes autoclave and pilot plant tests relative to the hydrocracking of the pine root oil fraction boiling from 185°C to 300°C. The product was a naphthenic fuel having an octane number of 90 to 94 with 0.15% added lead and was obtained in yields of 50% of the charged pine root oil fraction. The gasoline was superior in quality and yield to that obtained in catalytic cracking, but the latter process was adopted for future construction because of simplicity of design and ease of operation.

The hydrocracking plant at the Third Naval Fuel Depot, TOKUYAMA, was utilized in applying the results of the pilot plant tests. This unit treated 1.8 kiloliters per hour of charged oil and a yield of 71% of aviation gasoline was obtained. The conditions were as follows:

Hydrogen pressure..............	200 kg/cm^2
Temperature....................	400-450°C
Space Velocity.................	0.5-1.0
Catalyst.......................	NiO-MoO$_3$

A total of 600 kiloliters of pine root gasoline were prepared at TOKUYAMA by this process.

Part III
PROPERTIES OF PINE ROOT OIL PRODUCTS

The physical and chemical properties of the various pine root oils and gasolines are tabulated in Table I. Discussion of these products and more detailed information in regard to each will be found in Enclosures (A), (B), and (C).

Part IV
ENGINE TESTING OF PINE ROOT GASOLINES

Single cylinder engine tests on the untreated pine root oil fraction boiling below 185°C were conducted at the First Naval Depot and are reported in Enclosure (B)10. As would be expected the high gum content and low volatility rendered use of the fuel impracticable. When blended with ethyl alcohol, the fuel was also unsatisfactory. A blend of 80% (by volume) or alcohol with 20% of pine root oil gave test results comparable with those obtained using ethyl alcohol but the gum content of the fuel was exceptionally high.

The First Naval Technical Depot, YOKOSUKA, conducted full scale engine tests and flight tests on pine root oil gasolines which had been prepared at the First Naval Fuel Depot by catalytic cracking and by hydrocracking. Results were equivalent to those obtained with No. 1 grade aviation gasoline of 92 octane number. More detailed information on the test procedure and test results are given in Enclosure (B)11.

The blending of gasoline obtained by the catalytic reforming process with ethyl alcohol for use as a fuel for training planes was planned. The blending ratio was to be 60% (by volume) of pine root gasoline to 40% (by volume) of alcohol. No engine test data of this fuel were available.

Part V
RESEARCH ON RELATED PRODUCTS

Both the Army and Navy laboratories investigated the oils obtained from materials similar to pine roots with the purpose of including these materials in the same fuel program. The carbonization and the high pressure hydrocracking of pine resin were studied at the First Naval Fuel Depot (Enclosure (B)2 and (B)8). The Army Fuel Research Institute intended to utilize the dry distillation product of resin in the preparation of a fuel which was to be blended with alcohol. The resin was to be mixed with acid clay and dry distilled. The distillate was to be fractionated and the fraction boiling below 200°C was to be blended with alcohol. The properties of the pine resin gasoline before blending were as follows:

Specific Gravity, 15/4°C	0.82-0.83
Acid Value	0.2-0.4
Reid Vapor Pressure, kg/cm^2, 40°C	0.1
Gum Content, mg/100cc	3-4
Freezing Point, °C	Below-50
Engler Distillation	
First Drop, °C	60
10%, °C	130
50%, °C	170
90%, °C	195
Octane Number, unleaded C. F. R., Motor Method	75

Another project which was contemplated by the Army was the steam distillation of pine needles and the subsequent catalytic reforming of the product. The dry distillation of Shirakamba bark was also investigated. This material yielded 50% distillates in a process similar to that used for pine root oil. The yield of product was higher and the volatility characteristics were superior to those of pine root oil. The extraction of limonene from orange peel was also studied as a possible fuel source.

A summary of preliminary studies relating to the utilization of such materials as the trunks, branches and needles of acerose trees and the trunks and bark of broad leaved trees has been compiled by the First Naval Fuel Depot and is included as Enclosure (C).

Part VI
ECONOMIC ASPECTS OF THE PINE ROOT OIL PROGRAM

As can be readily concluded by a consideration of the various phases of the pine root oil program, it does not constitute a sound economic measure for obtaining aviation fuel. The plan called for the use of approximately 3,780,000 metric tons of pine roots per year and could not be maintained for more than two years. The yield of total pine root oil and tar was planned as 360,000 metric tons per year. This corresponds to slightly more than 400,000 barrels per year of aviation gasoline to be obtained by utilizing both the catalytic reforming and catalytic cracking processes.

The cost of obtaining the crude pine root oil is exceptionally high, although refining costs are nominal. It was estimated that the cost of 1 "to" (18 liters) of total pine root oil was 25.9 yen in November 1944. This represents a cost of 226 yen per barrel of crude oil. Most of this cost may be attributed to the expense of digging, transporting, and hand chopping the pine roots.

The Japanese technical personnel, who have studied and originated some of the procedures discussed in this report, are of the opinion that pine root oil can be utilized in Japan's post war economy as a source of such materials as menthol and camphor to be used for export. For this purpose, the Department of Commerce and Industry of Japan desires to stabilize the annual production of pine root oil at 10,000 kiloliters so that the pine tree resources may be preserved.

Table I
PROPERTIES OF PINE ROOT OILS

Description	Total Pine Light Fraction	Root Oil Heavy Fraction	Pine Root Oil Gasoline			
	-185°C	185-300°C	Contact Distillation	Catalytic Reforming	Catalytic Cracking	Hydrocracking
Specific Gravity	0.86	0.95	0.85	0.85	0.762	0.727
ASTM Distillation						
I.B.P. °C	110	165	70	70	44	36
10% °C	140	184		135	77	64
50% °C	170	234	160	165	105	101
97% °C	190	331(90%)	206	200	128.5	144
E. P.	250	332	210	280	172	175
Composition,%						
Unsaturates	89.2				11	0.5
Aromatics	6.8			60	32	12.9
Naphthenes	4.0			40	20.9	21.9
Paraffines					36.1	64.7
Octane Number						
Plain	70		80	85	75	71
Leaded(0.15%)	75		84	90	90	93

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ENCLOSURE (A)

ENCLOSURE (A)

THE PINE ROOT OIL RESEARCH PROGRAM AT THE FIRST NAVAL FUEL DEPOT, OFUNA

(In Two Parts)

by

DR. S. KOMATSU

CHEM. ENG. COMDR. H. FUJIMOTO

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (A)

LIST OF TABLES AND ILLUSTRATIONS

PART I

PART II

ENCLOSURE (A)

PART I

SUMMARY OF PINE ROOT OIL RESEARCH AT OFUNA

by

CHEM. ENG. COMDR. H. FUJIMOTO

INTRODUCTION

About 6000kl of pine root oil were produced in Japan in 1944, not including 8000kl of pine wood oil produced in Korea. These oils were used in solvents, flotation oils, drugs and cable oils, and also found applications in the rubber industry. No consideration had been given to use of pine root oil for fuel, except for studies on the dry distillation of terpene oil with acid clay by Prof. K. KOBAYASHI of Waseda University (Jour. Ind. Chem. Japan, Vol. 26, p. 463). A 158-161°C fraction of pine root oil was distilled with an equal amount of acid clay, and an oil having a petroleum like odour was obtained in yield of about 80% of the original feed. The reaction product contained 50% of olefines, and aromatics, and 50% of naphthenes. It was considered to be the decomposition product of intermediate polymers, produced by the action of clay on terpenes.

In August 1944, research on the dry distillation of pine wood and pine resin was started at the First Naval Fuel Depot, to meet the urgent demand for fuel, especially aviation gasoline. Laboratory experiments on this subject were made by Chem. Eng. Lieut. Comdr. M. KUMAMOTO (See Enc.(B)2), and the following results were obtained.

(a) The yield of tar increases with increase in heating temperature, and reaches a maximum at 440°C.

(b) The yield of tar and pyroligneous liquor increases and yields of charcoal and gas decrease with the increase of heating rate to 440°C.

(c) The yield of tar increases with age of the roots, giving best yields from roots over 60 years old.

The average yields of dry-distilled products from pine wood were found to be as follows:

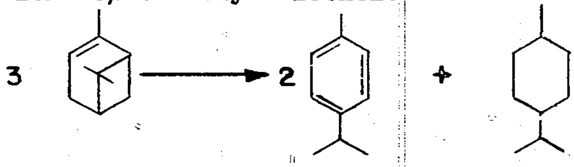
Tar	4.5 wt.% of wood.
Tar in pyroligneous liquor	5.0 wt.% of wood.
Acetic acid in pyroligneous liquor	1.2 wt.% of wood.
Acetone in pyroligneous liquor	0.1 wt.% of wood.
Methanol in pyroligneous liquor	0.4 wt.% of wood.
Charcoal	17.0 wt.% of wood.

Simultaneously with these experiments, designs of commercial plants were widely investigated from the standpoint of utilizing civilian techniques and avoiding large scale plants that would require long construction periods. Chem. Eng. Lieut. Comdr. R. YUMEN constructed several types of model retorts at OFUNA to compare their merits. Pilot plant tests on hydrocracking of pine root oil were also investigated.

ENCLOSURE (A)

The experiments on pine root oil retorting were continued by Chem. Eng. Lieut. Comdr. S. SANKA, and a KITAGAWA type retort was selected as the standard. This retort treats 350 kg of pine root per day and produces 10 kl of pine root oil per year. Data on commercial operations of this retort are reported in (Enc.(B)1). A plan for erecting 36,000 retorts all over the mainland and producing over 360,000 kl of pine root oil per year was proposed in December 1944. Marine forces helped in the construction and operation of the retorts, and in June and July 1945, production reached the planned figures.

All the personnel of this Depot concentrated on the producing and refining of pine root oil in order to obtain aviation gasoline, fuels and lubricants. Pilot plant hydrocracking and catalytic cracking tests to produce aviation gasoline from various fractions of pine root oil gave satisfactory results. (See Enclosures(B)5,(B)7, and (B)8). The aviation gasolines produced were subjected to flight tests at the YOKOSUKA Air Base. (See Encs.(B)10,(B)11) About 600 kl of hydrogenated aviation gasoline was produced on a commercial scale unit at the Third Naval Fuel Depot, TOKUYAMA. The construction of 21 small scale catalytic cracking plants, with a treating capacity of 10 to 30 kl of charge per day was planned (See Enc.(B)6), but was not accomplished. A research study of catalytic reforming was also completed (See Encs.(B)3,(B)4). The aim of this process was to minimize the gum content in the fraction boiling up to 185°C by the following reaction, and to use the product as an aviation gasoline after blending with 46% of ethyl alcohol.



PINENE P-CYMENE

Extensive construction of small simplified commercial catalytic reforming stills was started on sites near the pine root retorts, but only a few stills were completed by 15 August 1945.

GENERAL SUMMARY

The yield of pine root oil varies from 10 to 25% of the charge, according to the age of the pine roots. The products are usually separated into two parts, namely pine root tar from the tar separator and pine root crude oil from the receiver of the retort. These two distillates were produced in the ratio of 6:4, resp. Properties are as follows:

Pine Root Tar:

Sp. Gr. (20/15°C) 1.074
Completely soluble in 10% caustic soda.

Distillation (10mm Hg)

50 to 120°C	15.0%
120 to 150°C	3.0%
150 to 220°C	13.0%
Residue	69.0%

ENCLOSURE (A)

Pine Root Crude Oil:

Sp. Gr. (20/15°C)	0.974
n, (20/D)	1.5235
Ester value	62.9
E.V. after acetylation	91.3
Water soluble	8.5%
10% soda soluble	36.5%

Distillation:

below 150°C	4%
150 to 200	50%
200 to 300	23%
Residue	22%

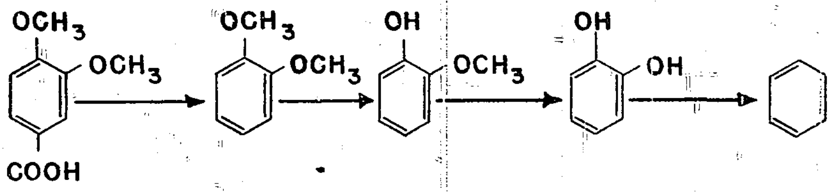
The above two oils were treated together as total pine root oil, because pine root tar solidifies in winter and is unsatisfactory for transportation.

Neutral oil, amounting to about 65% of pine root crude oil and about 16% of total pine root oil, has a density of 0.927, refractive index of 1.513, ester value of 29. This was fractionated as follows:

Temperature °C	Yield (Vol%)	Remarks
75 - 150	0.9	
150 - 190	51.6	Monoterpenes
190 -(130)8.5mm Hg	12.6	Terpene alcohol and sesquiterpenes
(130-200) 8.5mm Hg	16.0	Higher terpenes
Residue	17.0	Higher terpenes

S. AKIYOSHI (Report of OSAKA Technical Research Institute Vol. 17 No. 10(1937) found ℓ-α pinene with small amounts of dipentene, limonene and β-pinene in the monoterpene fraction, and longifolene with small amounts of β-terpineol and cadinene in the sesquiterpene fraction. Chem. Eng. Lieut. Comdr. H. SETO studied the corrosion of steel by pine root oil, and concluded that it was mainly due to the aliphatic carboxylic acids of C_3, C_4 and C_5 etc., in the lower boiling fractions. Corrosion by fractions boiling above 250°C was negligible.

T. HIRAIZUMI of the Takasago Perfumery Co. studied the action of acid clay on pine root tar and concluded that the tar consists of two major components. One of these is an aromatic acid containing carboxylic radicals, and some hydroxyl and methoxyl radicals, in the molecule; the other is abietic acid. By the action of acid clay, the former is decomposed as shown in the following formula:



and the abietic acid is changed to retene.

In preparing fuel oil from pine root oil, the oil is divided into three parts by distillation, i.e., the fractions, boiling below 185°C, 185°C to 300°C and residual oil. The residue, a viscous oil solidifing in winter, is subjected to further dry distillation to decompose the unstable components. The yields of these fractions are given in Figure 1(A).

The residual oil decomposes rapidly at 370°-390°C accompanied by violent foaming. Pilot plant tests showed that continuous pipe-still distillation was possible without any trouble at flask temperatures below 330°C. A small scale batch-type still was designed to operate distillation and dry distillation successively, based on the following two considerations.

It is necessary to construct commercial still near the pine root retorts and to avoid troubles which shall be due to foaming, caused by decomposition of tars.

Several pilot plant tests on high pressure hydrocracking and catalytic cracking (using various fractions of pine root oil) were carried out to obtain aviation gasoline. Experimental details are reported in Encs.(B)5,(B)7. The yields of of aviation gasoline are summarized as follows:

(a) Hydrocracking:

50 to 60 Vol% of charge using the fractions boiling below 250°C.

30 Vol% of charge using the fraction boiling from 185 to 300°C.

(b) Catalytic Cracking:

50 Vol% of charge using the fractions boiling below 185°C.

35 Vol% of charge recycling the fraction boiling from 185 to 300°C.

The gasoline obtained from hydrocracking is a naphthenic base gasoline and has an octane value of 92 to 94 with 0.15% of lead. The gasoline obtained by catalytic cracking is an aromatic base gasoline, having an octane number of 90 to 92 with 0.15% of lead. Although hydrocracking gives better yields and properties of product, catalytic cracking was adopted commercially since it was more suitable for rapid construction. Catalytic reforming of low boiling fractions of pine root oil, reported in Enc.(B)3 was also studied as a means of obtaining gasoline stocks which could be used as aviation gasoline after blending with ethanol. The overall scheme for production of aviation gasoline from pine root oil was planned as shown in Figure 2(A).

The dry distilled product had following properties and could be used in diesel or bunker oil.

Sp. Gr. (25/4)	1.020
Pour Point	-16°C
Flash point	77°C
Viscosity (R-2,20°C)	160 sec.
Conradson's carbon	0.67%
Ash	0.06%
Sediment	0.02%
Soluble in 10% caustic soda	20%

The cetane number of this product could not be determined by the C.F.R. engine, owing to misfiring.

Attempts to obtain lubricating oil from pine root oil will be unsuccessful because of its aromatic nature, but the methods reported in Enc.(B)17 are promising.

Research on preparing fuel from pine root oil was completed before the termination of the war. It is expected that pine root oil will become an important raw material for synthetic camphor and menthol, in the future.

ENCLOSURE (A)

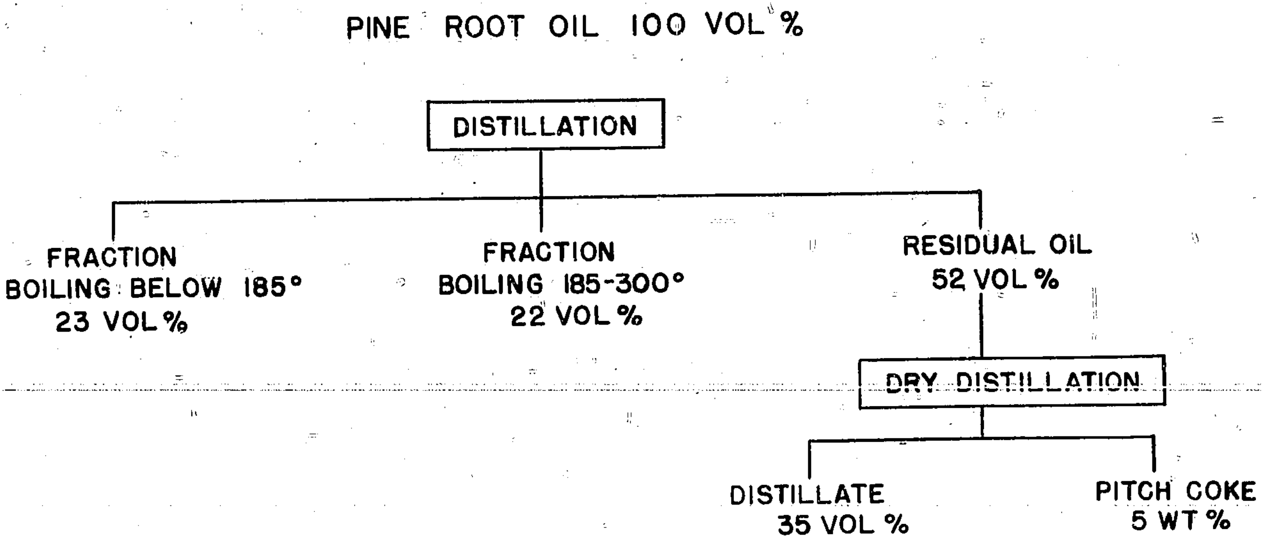


Figure 1(A)
YIELD OF FRACTIONS

ENCLOSURE (A)

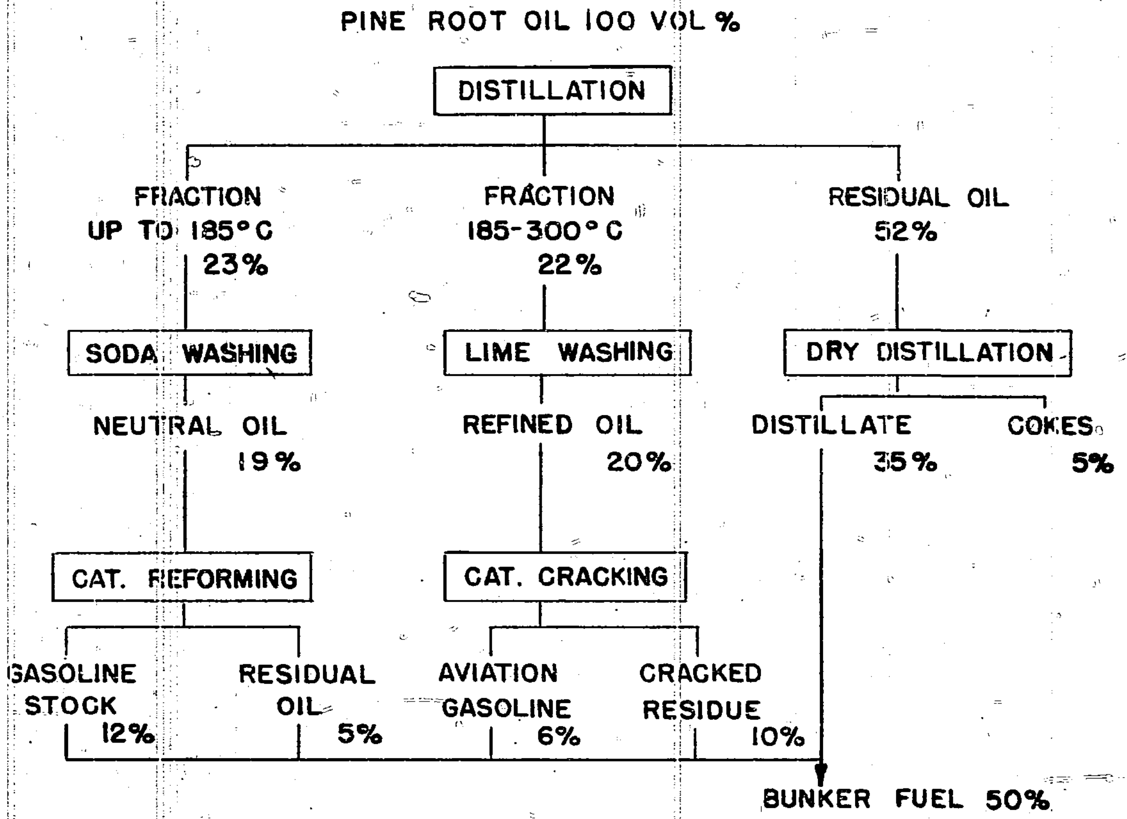


Figure 2(A)
OVERALL SCHEME FOR PRODUCTION
OF AVIATION GASOLINE FROM PINE ROOT OIL

ENCLOSURE (A)

PART II

CHEMISTRY OF PINE ROOT OIL

by

DR. S. KOMATSU

Chopped pine roots were dry-distilled by heating in a closed retort. The distillates were condensed separately in air cooled and water cooled vessels, and the liquid condensed in the former vessel was called "pine root tar". The condensate in the water cooled vessel after settling, separated into two layers, the upper consisting of pyroligneous acid and the lower consisting of tar. The pyroligneous acid contained "soluble tar" which could be separated by distillation. The two tarry matters were mixed together, and this was named "pine root crude oil". The yields of products were as follows:

Tar	19%
Pyroligneous acid liquor	25%
Charcoal	19%
Gas and loss	37%

The compositions of pine root tar and pine root crude oil are given in Table I(A). Since the ratio of tar to oil is 6:4, pine root oil consists of 74% acidic substances and 26% neutral substances.

Carboxylic fatty acids, constituting 10% of the acidic portion, are mostly included in the fraction boiling below 200°C. The remaining 90% consists of phenols, especially guaiacol derivatives. The phenol fraction of pine tar boiling between 190°C and 230° was examined by Renard, and the following constituents were found:

Mono phenols	40%
Guaiacol	20%
Cresol and homologues	37%

Resin acids compose 60% of the pine root tar, and are soluble in a 10% caustic soda solution.

The main part of pine root crude oil consists of neutral substances, such as ketones, furfural and its derivatives, terpenes, and aromatic compounds. The terpene and aromatic compounds are mainly pinene, camphene, dipentene, toluene, xylene and cumene.

Pine root oil, compared with coal tar, is richer in acidic substances and contains little or no sulphur compounds. The compounds in the oil should be related to the constituents of the raw material from which the tar is obtained. Hence, the root oil should contain various products formed by the pyrolysis of rosin, lignin and cellulose, the main composition of the roots. By analysis, the roots are assumed to contain 60% cellulose and other carbohydrates, 25% lignin, 10% rosin and 5% ash. By studying the exudations of pine wood, acidic resins and essential oils were found to be the two main constituents. (H. KUMAGAI; unpublished)

When cellulose and lignin were dry-distilled in a retort at 400°C, reaction products shown in Table II(A) were formed.

ENCLOSURE (A)

Acetic acid and its homologues, and furfural and its derivatives were produced by the carbonization of cellulose and sugars. These compounds were also obtained from pine root oil.

In spite of the extensive research on the chemistry of lignin, there still remain many obscure and controversial points. (M. Phillips, Chem. Rev., 14(1934), 103). It is, however, proved that an aromatic or, at least, a hydroaromatic nucleus is present, since a considerable amount of protocatechuic acid with some catechol and oxalic acid was obtained by the dry distillation of lignin. Thus, the source of the fatty acids and furfural and its derivatives can be definitely assigned to cellulose and sugars. The large amount of phenols and phenol ethers are formed from lignin, which is also the source of methyl alcohol in the tar, while the ketones are probably formed by a secondary decomposition of the fatty acids.

Pine root oil was fractionated into three fractions; namely, (1) below 185°C, (2) 185-300°C, (3) above 300°C. The first fraction, after washing with a dilute alkali solution to remove carboxylic acids, was subjected to either catalytic cracking or catalytic reforming. The former reaction was carried out at 450°C in the presence of an acid clay catalyst, and the latter at 350°C using the same catalyst. The gasolines produced by these two reactions were found to have the properties listed in Table III(A).

The 185-300°C fraction was washed with lime and then heated to 400-450°C, under hydrogen pressure of 200 atmospheres, in the presence of MoO_3 catalyst. The gasoline, obtained in a yield of 30% of the feed oil, had the following composition:

Aromatics	41%
Naphthenes	14%
Paraffins	27%

The octane value when leaded was 92-94.

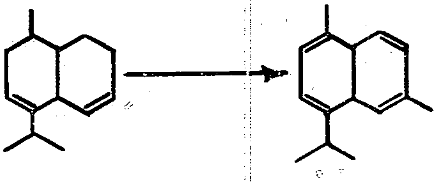
When the last fraction was distilled with acid clay at 400°C, the distillate contained 60% retene.

As is seen from the above experimental results, the aromatic content increases about 30%, while the naphthene content decreases, when each of the above fractions of pine root oil is treated with acid clay. From the experimental results obtained by HIRAIZUMI, an oil containing 18% phenolic compounds was formed by heating pine root tar to 400°C with 10% of acid clay, and the presence of benzene and guaiacoal was confirmed.

This fact indicates that the catalytic action of the acid clay on pine root oil increases the formation of aromatic compounds. Such phenomena have not been noticed in petroleum or coal tar chemistry, and remind one of the fact that, 23 years ago, S. KOMATSU, H. NAKAMURA and M. KURATO had noticed a sulfite terpene, obtained by cooking coniferous wood by the sulfite process, when working on sulfite pulp from Todomatsu wood. The terpene consisted mainly of p-cymene, and has been reported by P. Klason in his study of sulfite turpentine from western wood (Ber., 33, (1900), 2343). The formation of aromatic hydrocarbons from terpene, was considered to be due to oxidation by free sulphur which was formed during the cooking process, since pinene, when heated with 0.5% of sulphur at 200°C for 23 hours, produced about 50% of cymene. (J. Chem. Soc. Japan 45, (1923),496)

Furthermore, Ruzicka and his co-workers (Hel. 5, (1922), 345) succeeded in determining the structural formula of sesquiterpenes, using the Vesterberg process by converting the terpenes into cadalene or eudalene.

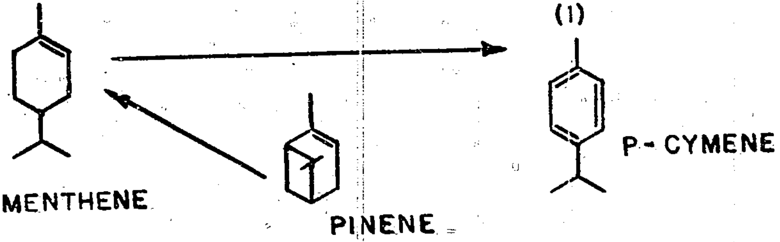
ENCLOSURE (A)



SESQUITERPENE CADALENE

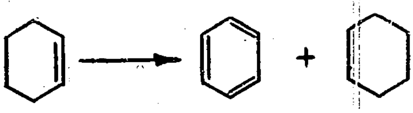
In 1903, Vesterberg (Ber. 36 (1903),4200) reacted pure abietic acid $C_{19}H_{29}CO_2H$ with sulphur, and obtained retene $C_{18}H_{18}$ as the chief product.

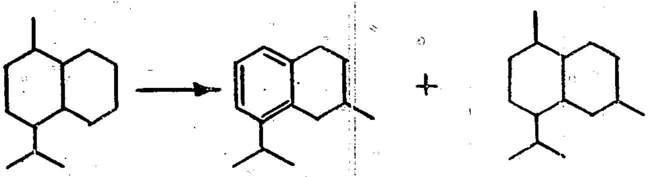
Terpenes show quite different chemical behaviours than the naphthenes in petroleum and coal tar. Cymene derivatives are produced by catalytic oxidation of terpenes, as shown in Scheme I. This characteristic behaviour of terpenes seems to depend upon their chemical constitution, i.e., hydrocymene derivatives.



One thing to be noticed in connection with the preceding paragraph, is the catalytic transformation of terpenes, investigated by S. KIMURA (Mem. Coll. Sc. Kyoto I.U.A. 14 (1931), 173). This reaction occurs in the catalytic reformation of pine root oil.

Catalytic auto-oxidation and reduction reactions of these compounds are well known or have been reported. Δ'-Dihydronaphthalene or octalin passed over palladium-asbestos heated to 250-300°C in a CO_2 atmosphere yields naphthalene and tetralin or tetralin and decalin. Sesquiterpene isolated from coniferous wood treated under the same reaction conditions as hydronaphthalene yields tetrahydro- and perhydrocadalene. The following catalytic oxidation-reduction reaction for cyclohexane has previously been noticed by N. Zelinsky and G. Pawlow (Ber., 57 (1924), 1066).

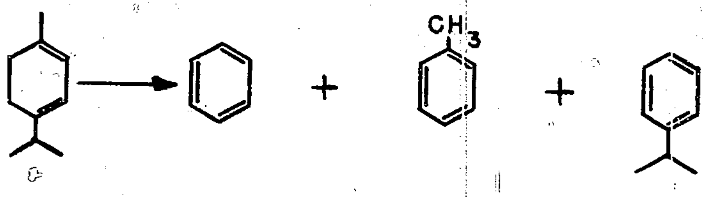




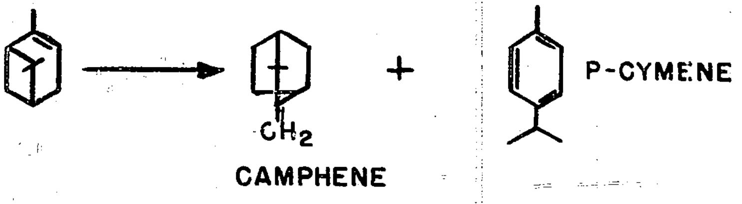
SESQUITERPENE TETRAHYDRO- PERHYDRO
CADALENE

p-Cymene has been decomposed into benzene, toluene and cumene, by the catalytic action of acid clay at 350-400°C, according to T. OKADA (unpublished).

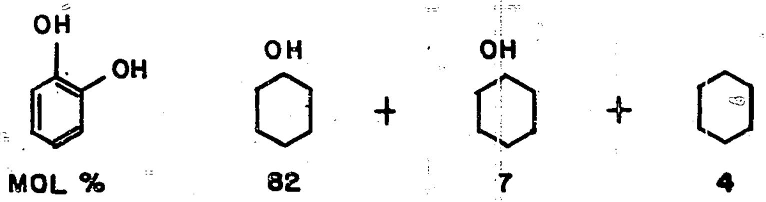
ENCLOSURE (A)

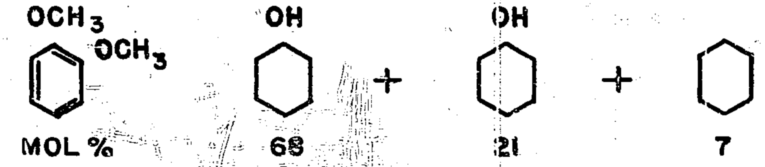


Pinene, under the same reaction conditions, changes to camphene and p-cymene.



Catechol and its derivatives, which are the aromatic compounds isolated from the decomposition products of lignin yield the following compounds by the catalytic action of reduced nickel under a high hydrogen pressure at about 200°C. (R. AMATATSU, J. Chem. Soc. Japan, 52 (1931), 585; S. FUJITA, ibid. 60 (1939), 296)





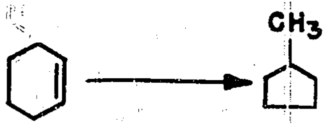
Toluene, benzene and phenol have been formed by thermal decomposition of cresols (R. NAKAI, Bull. Chem. Soc. Japan 5 (1930), 136), as a result of demethylation. The case of demethylation from benzene nuclei is in the order para, ortho, meta. The methyl or hydroxyl group in phenol derivatives, situated in the meta position to a hydroxyl group can most easily be removed by catalytic hydrogenation.

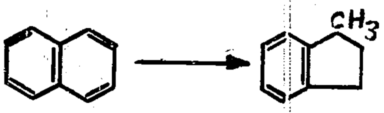
The above mentioned experimental results are characteristic of the chemical changes which occur in the catalytic cracking or catalytic reforming of pine root oil.

The chemical reactions occurring in the hydrocracking of pine oil at high temperatures and high hydrogen pressure were investigated by M. HAGIWARA. Experiments were made with bicyclic terpenes at high temperature and high hydrogen pressure, in the presence of reduced nickel. The following results were obtained, (1) menthene was changed to menthane, (2) pinene was converted to pinane and then to menthane, (3) camphene was changed to camphane and then was decomposed to open chain paraffin hydrocarbons with fewer carbon atoms, (4) menthane was partly decomposed to paraffin hydrocarbons and the remainder dehydrogenated to p-cymene. (unpublished)

ENCLOSURE (A)

In order to endow the pine root oil gasoline with the same fuel characteristics as that of petroleum, it appears that, from the chemical standpoint, the presence of some compounds of the pentamethylene series is necessary. Fortunately, pine root oil contains terpenes that can be changed to isomeric pentamethylene compounds by intramolecular rearrangement, according to the investigations on cyclohexene and dihydronaphthalene made by M. HAGIWARA. (unpublished) The reactions are based on the catalytic action of alumina at 300°C, and isomeric pentemethylene derivatives are formed as follows:


CYCLOHEXENE METHYLCYCLOPENTANE


METHYLINDANE

Thus, terpenes are either converted to aromatic and hydroaromatic compounds by catalytic transformation, or to isomeric pentamethylene derivatives by intramolecular rearrangement. The exact chemical reactions to be encountered with terpenes, depend on the experimental conditions and the nature of the catalyst. Determination of the optimum conditions and selection of satisfactory catalysts are questions to be settled in the near future. Studies on the Raman spectra and ultra-violet ray absorption spectra of terpenes will also be of value in solving these problems.

ENCLOSURE (A)

Table I(A)
COMPOSITIONS OF PINE ROOT TAR AND PINE ROOT CRUDE OIL

	Pine Root Tar	Pine Root Crude Oil
Acidic substances	100%	36%
Neutral substances		64%

Table II(A)
REACTION PRODUCTS, DRY-DISTILLATION OF CELLULOSE AND LIGNIN

	Cellulose (%)	Lignin (%)
Tar	23	13
Aqueous Liquor	33	12
Gas	25	18
Cokes	17	57

(S. KOMATSU, "Biochem. Studies on Rice Bran Tar" Mem. Coll. Sc. K. I. U., A. 11 (1928), 481).

Table III(A)
COMPARATIVE RESULTS, CATALYTIC CRACKING AND REFORMING

	Gasoline	
	From catalytic cracking	From catalytic reforming
Aromatic content	32%	60
Naphthene content	21%	40
Octane Number (0.15% added lead)	90-92	90-94

RESTRICTED

ENCLOSURE (B)

ENCLOSURE (B) 1

DESIGN STUDIES
OF CARBONIZATION APPARATUS
FOR PINE ROOTS

by

NAV. CHEM. ENG. LIEUT COMDR.
S. SANKA

Research Period: 1944-1945

Prepared for and Reviewed with Author by
U. S. Naval Technical Mission to Japan.

December 1945

ENCLOSURE (B)1

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)1

I. INTRODUCTION

A. History

Pine root oil has been manufactured in our country for many years. The carbonization of pine roots is a domestic industry, and the operation a very expensive one. Under ordinary conditions it would not be a successful method of producing fuels. In September 1944, however, this industry was expanded as the result of war time necessity, and the design of a simplified unit for carbonization of pine root was given high priority. In this connection, a visit was made to NAGANO Prefecture for the purpose of inspecting, and sketching pine root installations. These installations had daily carbonization capacities of 500 - 750 kg of pine roots and consisted of 2 vertical retorts. On the basis of this survey and other considerations, it was decided to design according to the following conditions:

1. The construction of the apparatus would be as simple as possible using a minimum of critical materials.

2. The retorts would be of the vertical type with a daily charge capacity of 375 kg of pine roots each.

After this apparatus was designed, in December 1944 experiments were made to study the following:

1. Temperature distribution in the retort.

2. Relation between firing and distillate.

3. Comparison of "A" and "B" type distillation units as shown in Figure 5(B)1.

On the basis of these experiments, type "A" apparatus was adopted for large scale installations.

B. Key Research Personnel Working on the Project

Nav. Eng., T. SHIBAZAKI
Nav. Chem. Eng. Lt. Comdr., S. SANKA
Nav. Chem. Eng. Lt. (jg), Y. MORI
Nav. Chem. Eng. Lt. (jg), H. KINGO
Nav. Ass't. Eng., M. KUBOTA

II. DETAILED DESCRIPTION

A. Design and Operating Procedure

A flow sheet of the plant is shown in Figure 1(B)1. The pine roots are cut into pieces about 2.5 cm^2 and 30 cm in length, and 270-380 kg are packed into the retort. After about 2 hours of firing, the oil and pyroligneous liquor flow from the condenser and are separated into two layers in the water separator. Tar is separated in the tar-separator and is collected in the tar receiver after about 3.5 hours of firing. Gas produced after about 5.5 hours of firing is used as fuel.

B. Experimental Results

1. Yield and material balance (based on 375 kg charge of pine roots). See Table I(B)1.

The yield was much affected by the quality of pine roots. Between rich and poor pine roots, there was a range from 8 to 40% by wt. yield of tar plus oil, the average yield being about 20%. Under actual operating conditions the yield was very much influenced by leakage at the joints of the bamboo cooler. Painting the joints with boiled tar was tested, but when the temperature reached 30°C this was not effective.

2. Properties of product. See Table II(B)1.

3. Performance data. The relations between yield of distilled oil, fuel consumption and time is shown in Figure 2(B)1. The temperatures distribution in the retort and the effect of water content of the charge, on the carbonization pine stems was also studied and the results are given in Figure 3(B)1 and Figure 4(B)1. Labor and utility requirements are summarized below:

Operating Cycle

Carbonization of pine roots.....	10 -12 hr
Cooling of retort...............	8 - 9 hr
Preparation and charge..........	3 hr
Total	18 - 24 hr

Fuel Consumption

Wood (Using gas from carbonization retort).
100-150 kg/retort/day.

Condensing Water

Cooling water (average)
$1\ m^3/hr \times 13 hr/day = 13\ m^3/day$
for 2 retorts.

Labor

Chipping pine roots.................	6 men
Fire man	1
Oil receiver man....................	1
Total	8

III. MISCELLANEOUS DESIGN CONSIDERATIONS

A. Basis for Selection of the Vertical Retort--(Type A).

1. Professional pine root workers had used the vertical type retort more than the horizontal type. Accordingly, to develop the dry-distillation method most rapidly, it was considered best to use the vertical type.

2. It was generally believed that to get terpene oil of good quality from pine roots containing much resin, the vertical type retort was more suitable than the horizontal due to less oil cracking.

3. A retort of 375 kg (100 kan) was adopted since this size could be made simply by rolling a 5 ft x 10 ft steel plate and welding.

ENCLOSURE (B)1

From the standpoint of yield, a smaller retort would be slightly better, but on the basis of labor requirements, working hours and actual quantity of oil obtained, the 5 ft x 10 ft retort was superior.

B. Comparison of Two Types of Carbonization Apparatus

Two types of dry-distillation retorts as shown in Figure 5(B)1 were studied. Test runs were made and results are tabulated in Table III(B)1. The temperature distribution in each retort is given on Figure 5(B)1. On the basis of these experiment it was concluded that "A" type is more efficient than the "B" type.

C. Basis for Selecting Bamboo for Cooling Pipe

1. There was a shortage of copper and iron pipe in Japan, and bamboo was conveniently available.

2. The cooling effect of bamboo was fairly good, the overall heat transfer coefficient being approximately 30-40 kcal/m^2/hr/°C as compared with 60 for iron pipe.

Table I(B)1
YIELD AND MATERIAL BALANCE

Product	Quantity		Wt % based on charge
	Liters	Kg	
Gas and loss			15
Pyroligneous liquor	150	165	44
Pine root crude oil	27	26	7
Pine root tar	45	54	14
Pine charcoal		75	20
Total	222	320	100

ENCLOSURE (B)1

Table II(B)1
PROPERTIES OF PRODUCT

		Crude oil	Tar	Oil and tar mixed
Specific gravity		0.964	1.070	0.990
Distillation (°C)	Initial point - 150	3.4	4.0	3.7
	150 - 200	50.5	5.8	31.0
	200 - 250	11.2	6.0	12.1
	250 - 300	11.2	9.0	7.1
	300 - 330	10.3	55.5	25.5
	Residue in 100cc (gm)	19.1	15.2	19.0

Table III(B)1
TEST RUN RESULTS

	Charge of Pine roots	Operating hours	Fuel consumption (wood charcoal)	Yield of tar and oil*	Cooling time** hours
Type A	300 kg	10-12	60-80 kg/cycle	about 20%	4-6
Type B	300 kg	12-14	80-100 kg/cycle	about 20%	9-12

* Weight per packed pine root

** Cooling time: The retort must be cooled to below 150°C before opening to prevent combustion of the charcoal.

ENCLOSURE (B)1

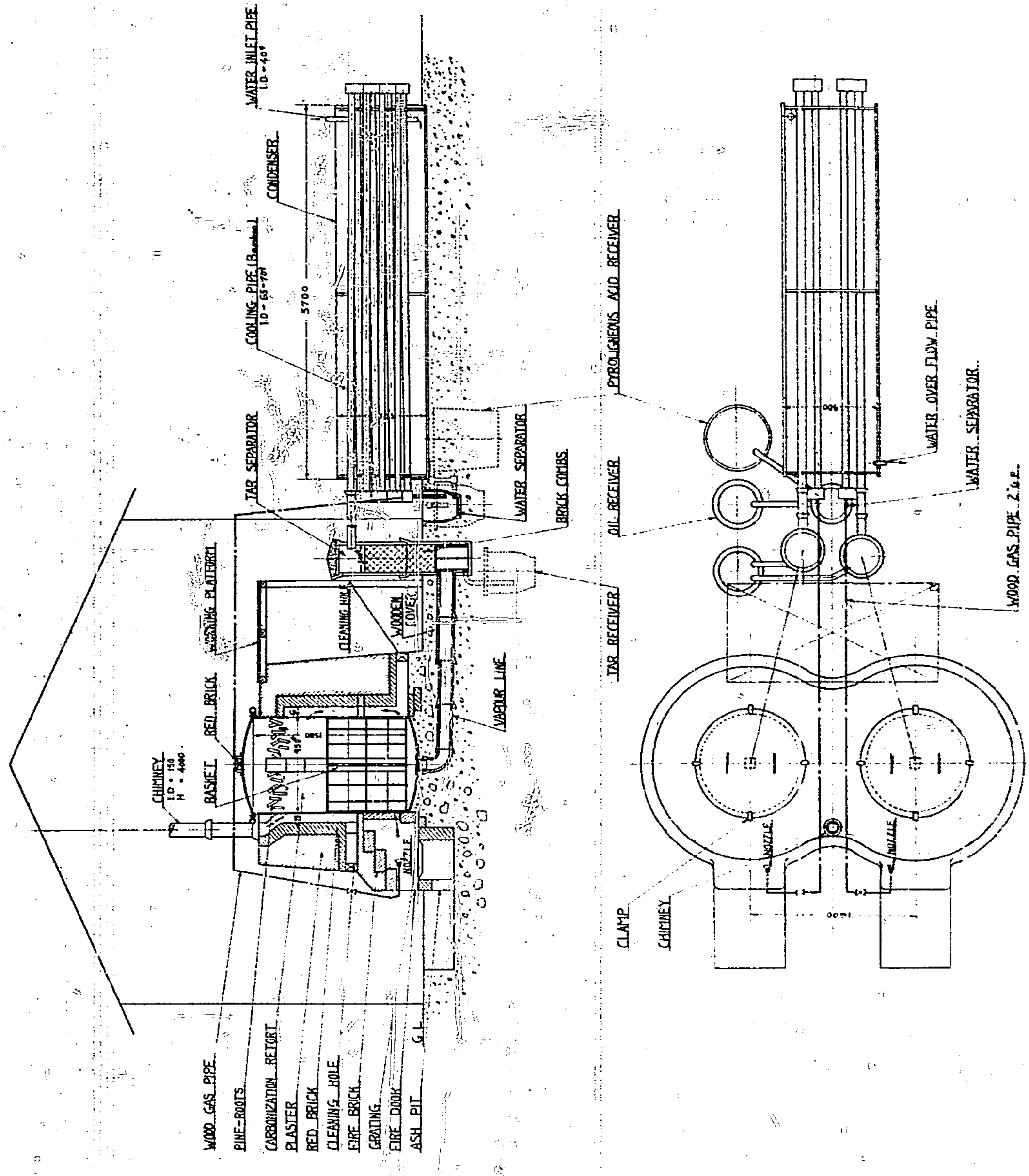


Figure 1(B)1
GENERAL ARRANGMENT OF PINE-ROOT CARBONIZATION APPARATUS
Daily Capacity 750kg/1set.

ENCLOSURE (B)1

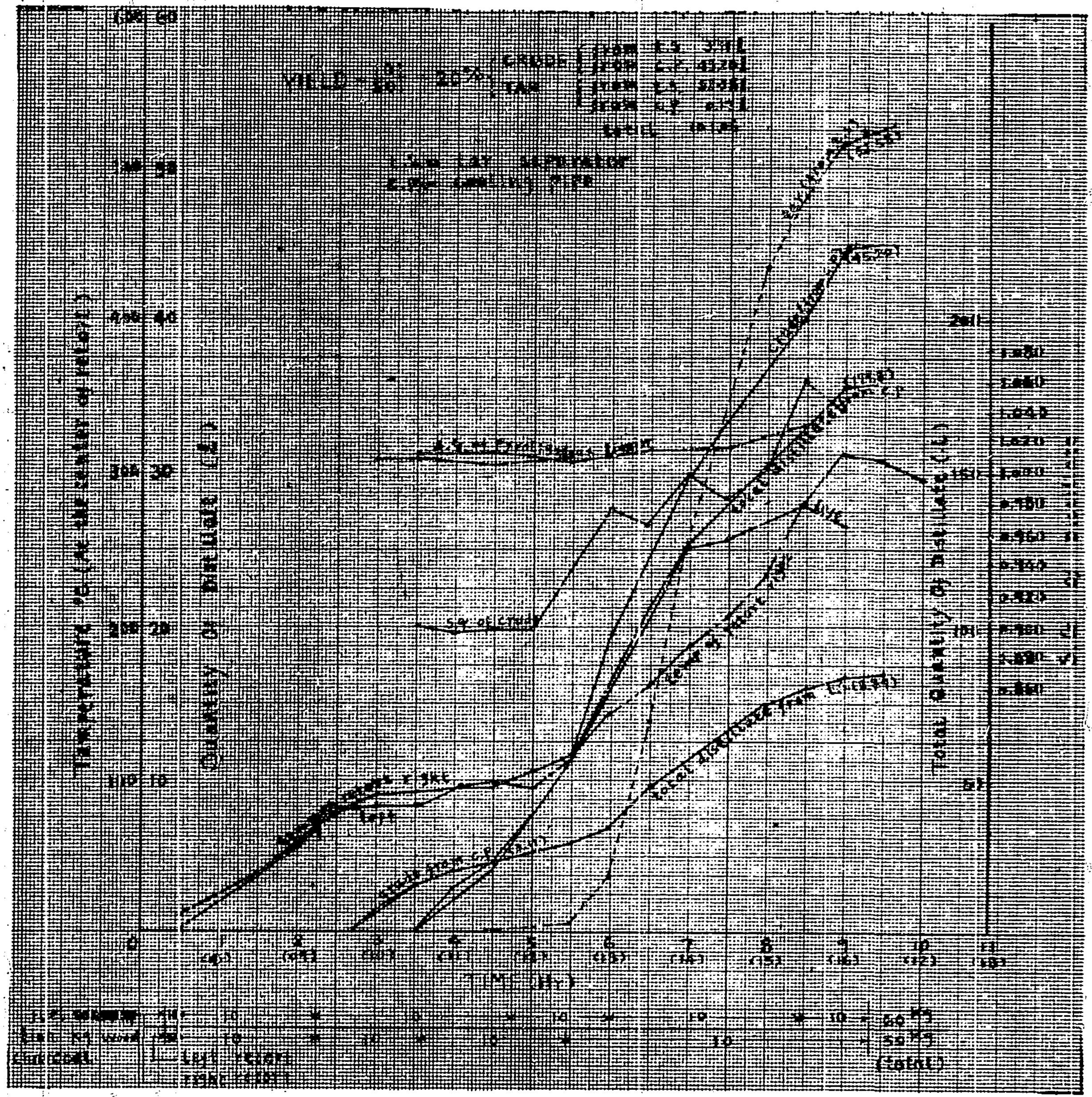
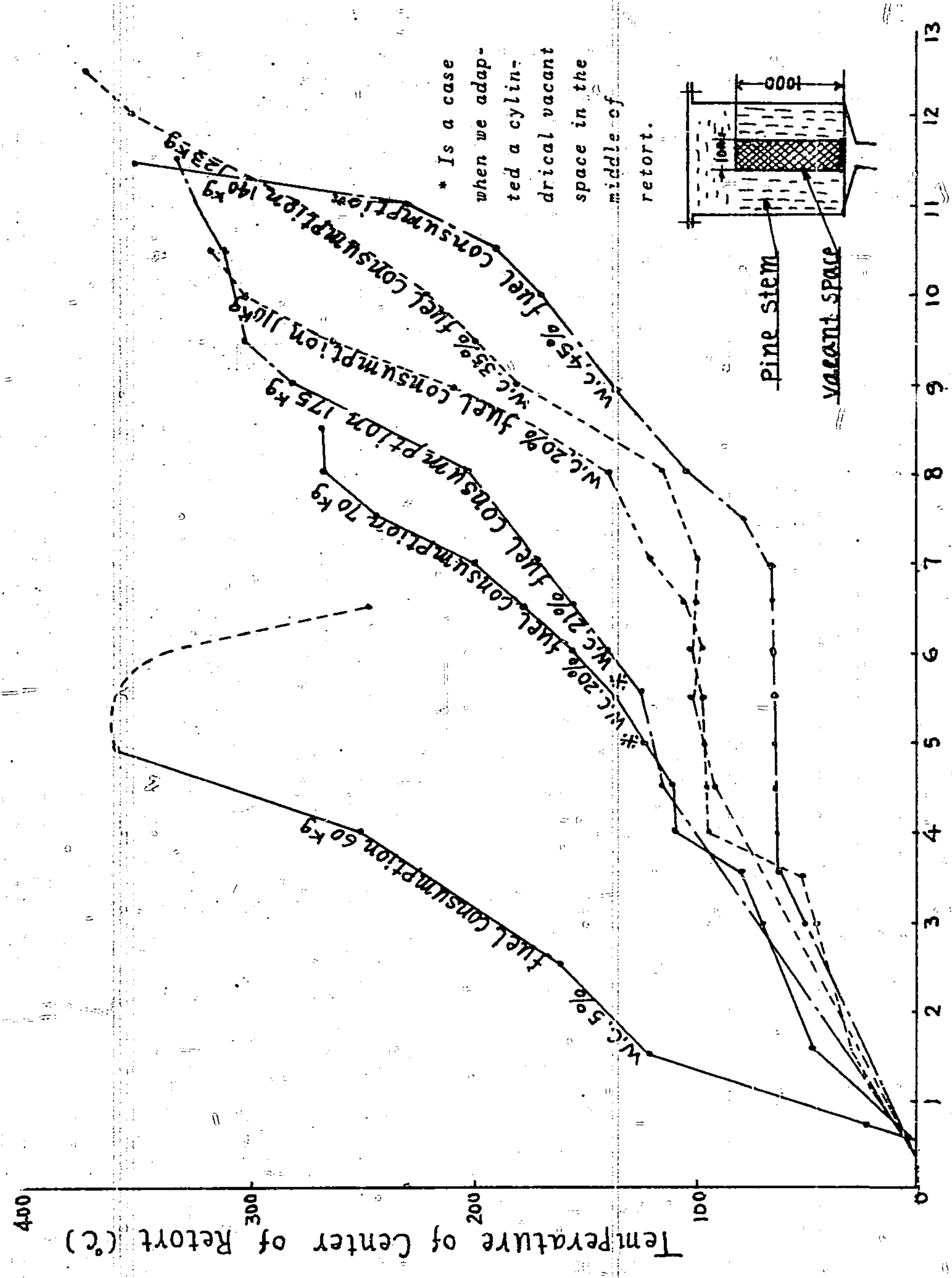


Figure 2(B)1

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.



* Is a case when we adapted a cylindrical vacant space in the middle of retort.

Figure 3(B)1

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

ENCLOSURE (B)1

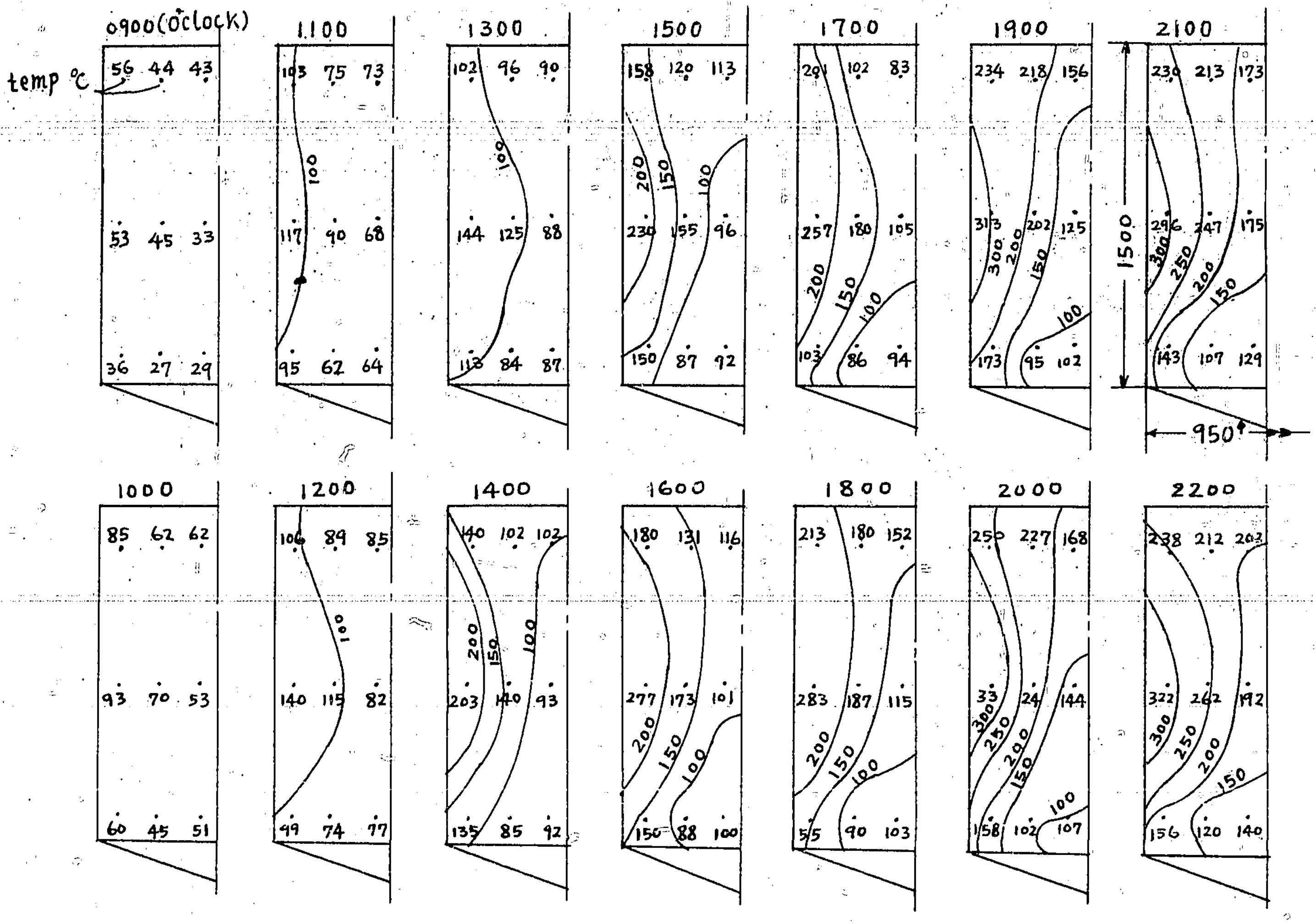


Figure 4(B)1
THE CHANGE OF THE TEMPERATURE DISTRIBUTION
IN THE RETORT (USED THE PINE STEM) ('A' TYPE RETORT)

ENCLOSURE (B)1

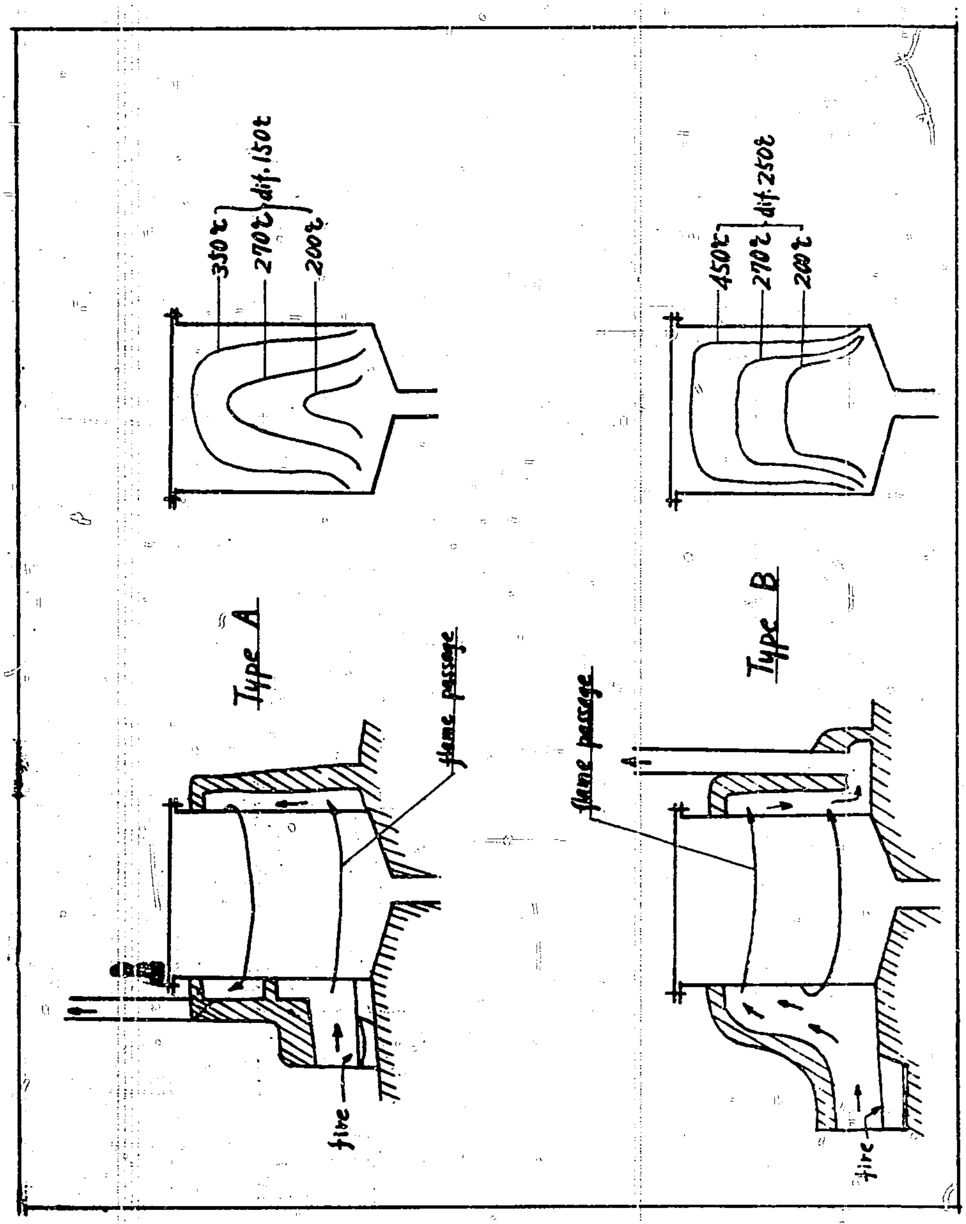
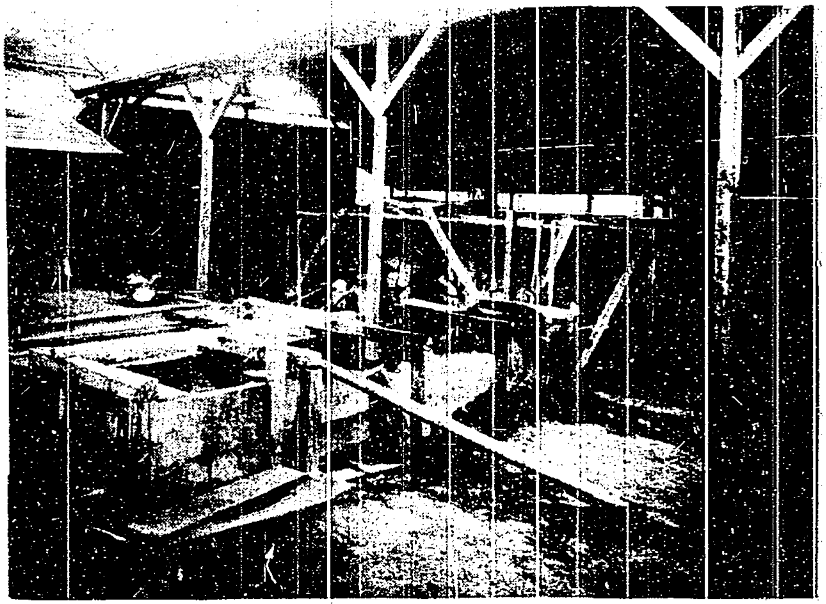


Figure 5(B)1
THE COMPARISON OF A AND B DISTILLATION APPARATUS

ENCLOSURE (B)1

Figure 6(B)1
TYPICAL VIEW
OF PINE ROOT
CARBONIZATION
FACTORY IN
THE COUNTRY

Figure 7(B)1
TYPICAL VIEW
OF PINE ROOT
CARBONIZATION
FACTORY IN
THE COUNTRY



ENCLOSURE (B)2

STUDIES ON THE CARBONIZATION OF RESIN

by

CHEM. ENG. LIEUT. COMDR.
M. KUMAMOTO

Research Period: 1944-1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)2

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)2

SUMMARY

This work was carried out to obtain as much aviation gasoline and boiler fuel from pine resin as possible.

The effect of wood charcoal or acid clay on the carbonization of resin was investigated. The decomposition temperature was lowered by acid clay but wood charcoal was not as effective. The acid value and saponification value of the distillates was lowered by use of these catalysts. Higher compounds were converted by acid clay into lower compounds but wood charcoal did not have this effect and served only to facilitate the breaking of the C-COOH bond.

The distillate obtained by the carbonization with wood charcoal was fractionated in 3 fractions. The first fraction (I.D. to 185°C) was treated by catalytic reforming and about 64% of aviation gasoline suitable for blending was obtained. The 2nd fraction (185 to 300°C) was treated by catalytic hydro-cracking and about 40% of aviation gasoline was obtained. The 3rd fraction (over 300°C) was examined and found to have the general properties of boiler fuel.

I. INTRODUCTION

A. History of Project

The essential components of crude pine resin are mono-, sesqui-, and diterpenes and related derivatives. It was thought that the C-COOH bond in abietic acid would be broken easily by thermal energy and the resin would be changed into a liquid. Therefore, the carbonization of resin and the utilization of the liquid product for aviation gasoline was studied. This investigation was started in Nov. 1944 and was not completed.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. Comdr. M. KUMAMOTO
Chem. Eng. Sub-Lieut. F. HOSINO

II. DETAILED DESCRIPTION

A. Test Apparatus

1. The test apparatus for carbonization is shown in Figure 1(B)2. Remarks:

T_1 = Thermometer
T_2 = Thermocouple
F = Distillation Flask
H = Heater
C_1, C_2 = Condenser
G = Gas meter
R = Receiver for distillate

B. Procedure

A charge of 1 kg of resin and 300gm catalyst was introduced into the distillation flask. Heating was regulated by a regulator. As the temperature increased, gas was evolved and measured by the gas meter. Gases obtained at different temperatures were analysed by the Hempel apparatus, and the distillates were fractionated in 3 fractions, the 1st fraction had a boiling range from initial drop to 185°C, the 2nd was 185°C to 300°C and the last was over 300°C. For each fraction the acid value, saponification value and physical properties were determined.

1. Catalytic Reforming

The 1st fraction was treated by catalytic reforming, and the octane value of the fraction of reformed gasoline boiling below 200°C was determined.

2. Catalytic Hydro-cracking

The 2nd fraction was treated by catalytic hydro-cracking. A 2.4 liters capacity autoclave was used. 300gm of sample and 15gm of mixed catalyst (3 parts of Ni-oxide, 1 part of MoO_3 and 3 parts of acid clay) were placed in the apparatus. After purging the air with hydrogen gas, the pressure of H_2 was raised to 100 kg/cm². About 7 hours were required to heat up to 450°, and the autoclave was kept at that temperature for 1 hour. After cooling, the products were removed and the properties of the aviation gasoline obtained were determined.

C. Experimental Results

The physical and chemical properties of crude pine resin obtained from SHIZUOKA Prefecture are as follows:

Sp.Gr. (30/4)	1.012
Acid value	92
Saponification value	111
Solid impurities, %	3.1
Moisture, %	4.0

1. Dry-distillation of pine resin

The experimental conditions and results are given in Table I(2). The decomposition of resin was observed to occur at 300°C and to give a quantitative yield of carbon dioxide and methane. The amount of carbon dioxide decreased with increasing temperature and the methane evolved increased. The analyses of the gases evolved at different temperatures are shown in Table II(B)2. It appears that the deoxygenation and demethylation reaction started to occur at 300°C or higher. However, the 185-300° fraction of pine resin was not decomposed during this distillation. The physical and chemical properties of the distillate are given in Table III(B)2. The acid value of the fraction boiling from 185 to 300°C is much higher, comparatively, than that of the other fractions. This is due to the carrying over of undecomposed acidic substances.

2. Catalytic Dry-distillation

a. Effect of wood charcoal

Carbonization of resin in the presence of about 30% of wood charcoal was carried out. The results are tabulated in Tables IV(B)2, V(B)2, and VI(B)2. Cracking, mainly the evolution of CO_2 occurred at 300°C as was the case in the dry distillation. The effect of wood charcoal on the carbonization was not

ENCLOSURE (B)2

appreciable but it did decrease the decomposition temperature and, by adsorption, tended to slow down the distillation of the 185°-300°C fraction.

b. Effect of acid clay

In the carbonization of resin in the presence of acid clay the ratio of acid clay to resin was 3:10. The experimental procedure was similar to that using wood charcoal. The results are tabulated in Tables VII(B)2, VIII(B)2, and IX(B)2. The 1st reaction occurred at 200°C and is thought to be mainly the decomposition of the C-COOH bond. The 2nd reaction taking place at approximately 320°C was that of de-isopropylatio since the gases obtained at that temperature were compose chiefly of unsaturated hydrocarbons. The acid clay was very effective since the acid value of the distillate was less than 1. The decomposition temperature was lowered, the sesquiterpene alcohols were dehydrated, and the C-C ring bond was broken.

3. Catalytic Reforming

The charging stocks were fractions boiling from the initial boiling point to 185°C from the charcoal catalyzed experiment, and the terpene fraction obtained by steam distillation of crude resin. The general properties are given in Table X(B)2.

Experimental conditions were as follows and the results are tabulated in Table XI(B)2.

Sample treated.	about 1.01
Reaction Temperature.	400°C
Catalyst.	acid clay
Space Velocity.	1.0

4. Catalytic Hydro-cracking

The experimental conditions of catalytic hydro-cracking were as follows:

Reaction Temperature.............	450°C
Sample treated...................	300cc
Catalyst.........................	No. 105
Reaction time....................	1 hour
Apparatus........................	Rolling type Autoclave
Initial Pressure kg/cm^2.........	100
Reaction Pressure kg/cm^2.........	200

About 40% aviation gasoline was obtained, and the general properties of this aviation gasoline are tabulated in Table XII(B)2.

5. Properties of the Fraction Over 300°C

The general properties of the fraction boiling over 300°C were investigated and are as follows:

Sp. Gr. 25/4.	0.9740
Flash point °C	131
Freezing point °C	below -15°C
Viscosity at 0°C sec	
Redwood No. 1	327.8

Ash (%)..................... trace
10% NaOH soluble (%) 2.0
Water (%)..................... 0.03
Acid value..................... 1.49
Sap. value..................... 4.24

This fraction is suitable for use as a boiler fuel.

III. CONCLUSIONS

1. In the distillation of pine resin the C-COOH bond will be broken by keeping the resin at 300°C or higher and the reaction temperature will be lowered by the presence of catalysts such as acid clay.

2. Wood charcoal does not serve to lower the acid value of the 185 to 300°C fraction.

3. Acid clay serves the following purposes:

   a. The deoxygenation & dehydration reaction occurs at 200°C.
   b. With increasing temperature CO and unsaturated hydrocarbons are the chief components of the evolved gas, and the higher molecular weight compounds of **resin** are converted into compounds of lower molecular weight.

4. By catalytic reforming, high octane value gasoline is obtained but the distillation curve is not suitable for aviation fuel, therefore the gsoline can be used only for blending.

5. By catalytic hydro-cracking a high quality aviation gasoline is obtained.

6. The fraction above 300°C which is obtained by carbonization of resin would be useful as boiler fuel.

Table I(B)2
YIELD OF THE PRODUCT

	Exp. No.	
	4	5
Max. Temp., (°C)	395	367
Time, hours	10.5	6.3
Oil Yield, (%)	52.0	76.0
Residue, (%)	2.5	10.5
Water, (%)	3.1	3.5
Gas & loss, (%)	12.4	10.1
Gas evolved, l	57.0	56.7

ENCLOSURE (B)2

Table II(B)2
COMPOSITION OF GASES EVOLVED

	Ex. No.						
	4			5			
Temp. (°C)	300	310	330	310	330	350	360
CO_2 (%)	44.3	43.4	36.1	49.1	39.9	17.4	17.6
O_2 (%)	0.4	0.4	0.7	0.2	0.7	0.4	0.5
C_nH_n (%)	3.0	3.7	4.6	3.3	4.2	5.0	3.5
CO (%)	0.0	0.0	2.1	0.0	3.9	25.1	1.6
H_2 (%)	0.0	1.4	0.0	1.9	0.0	0.0	0.0
CH_4	54.2	45.3	54.8	43.6	46.9	50.5	57.6

Table III(B)2
THE YIELD & THE PROPERTIES OF EACH FRACTION

Boiling Range of Fraction		Exp. No.	
		4	5
I.D. to 185°C	Yield to distillate (%)	28.6	30.8
	Sp. Gr. (25/4)	0.8536	0.8618
	n_D^{15}	1.4610	1.4590
	Acid Value	1.18	1.97
	Sap. Value	6.79	3.78
185°C to 300°C	Yield to distillate (%)	28.2	32.4
	Sp. Gr. (25/4)	0.9488	0.9491
	n_D^{15}	1.5050	1.4840
	Acid Value	29.84	33.92
Over 300°C	Yield to distillate (%)	43.02	36.6
	Sp. Gr.	0.9914	0.9845
	Acid Value	20.29	25.13
	Sap. Value	23.18	25.58

ENCLOSURE (B)2

Table IV(B)2
YIELD CF PRODUCT
(Wood Charcoal Catalyst)

	Exp. No.	
	8	9
Time, hours	8	6.8
Oil Yield (%)	72.3	73.0
Residue (%)	20.0	17.0
Water (%)	5.1	5.5
Gas & Loss (%)	2.6	4.5
Gas, 1	58.0	62.8

Table V(B)2
ANALYSES OF EVOLVED GASES
(Wood Charcoal Catalyst)

	Exp. No.							
	8				9			
Temp. (°C)	300	340	380	410	300	340	380	410
CO_2 (%)	46.5	19.1	15.3	9.6	48.0	21.7	15.4	17.5
O_2 (%)	0.9	0.7	0.2	0.7	0.7	0.5	2.5	0.5
C_mH_n (%)	2.5	5.4	5.7	6.0	3.1	4.8	5.1	5.2
CO (%)	11.6	28.7	19.7	13.6	5.0	18.8	11.0	10.7
H_2 (%)		0.0	18.9	23.3	3.7	0.0		
CH_4 (%)		42.3	38.8	51.2	36.7	53.5	57.4	56.8

Table VI(B)2
PROPERTIES OF CARBONIZATION PRODUCTS
(Carbonized in Presence of Wood Charcoal)

		Exp. No.	
		8	9
Crude oil Distillated	Sp. Gr.(25/4)	0.9273	0.9332
	n^{15}_{D}	1.4975	1.5000
	Acid Value	23.72	27.53
	Sap. Value	27.08	32.90
B.P. from I.D. to 185°C	Yield (%)	40.8	36.0
	Sp. Gr.(25/4)	0.8465	0.8413
	n^{15}_{D}	1.4604	1.4581
	Acid Value	4.36	5.43
	Sap. Value	8.77	6.40
B.P. from 185°C to 300°C	Yield (%)	10.0	11.3
	Sp. Gr.(25/4)	0.9157	0.9162
	n^{15}_{D}	1.4930	1.4945
	Acid Value	13.33	16.56
	Sap. Value	21.39	33.22
B.P. over 300°C	Yield (%)	49.2	52.7
	Sp. Gr.	0.9984	0.9525
	Acid Value	18.45	32.40
	Sap. Value	32.36	36.37

ENCLOSURE (B)2

Table VII(B)2
DISTILLATION YIELDS
(Acid Clay Catalyst)

	Exp. No.	
	11	12
Time, hours	6.8	6.8
Oil (%)	73.8	72.5
Residue (%)	6.5	5.0
Water (%)	11.0	11.2
Gas & Loss (%)	8.5	11.3
Gas, l	94.0	93.6

Table VIII(B)2
GAS ANALYSES
(Acid Clay Catalyst)

	Exp. No.														
	11							12							
Temp. (°C)	300	250	300	340	380	420	450	200	220	250	300	320	340	380	420
CO_2 (%)	43.5	13.2	4.2	4.5	3.8	2.7	2.8	12.3	50.4	11.2	7.4	4.3	2.6	1.6	1.9
O_2 (%)	0.6	0.6	1.0	0.3	0.8	1.7	2.2	0.2	0.7	2.3	0.6	0.7	0.8	0.4	0.5
C_mH_n (%)	3.1	7.1	43.4	32.1	12.8	8.9	6.2	3.8	2.9	5.5	0.8	41.4	47.3	23.8	16.1
CO (%)	41.3	37.0	0.0	0.0	0.0	0.0	0.0	50.7	25.1	52.6		0.0	0.0	0.0	0.0
CH_4 (%)	10.9	38.6	47.1	59.8	66.8	70.7	78.4	30.3	20.0	24.6	42.9	53.6	43.6	69.1	70.5
H_2 (%)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

ENCLOSURE (B)2

Table IX(B)2
PROPERTIES OF THE DISTILLATE
(Acid Clay Catalyst)

		Exp. No.	
		11	12
Crude oil distillated	Yield	73.8	72.5
	Sp. Gr.	0.9002	0.8901
	n^{15}_{D}	1.4880	1.4850
	Acid Value	0.39	0.32
	Sap. Value	8.57	3.42
B.P. from I.D. to 185°C	Yield	32.0	32.0
	Sp. Gr.	0.8003	0.8116
	n^{15}_{D}	1.444	1.447
	Acid Value	0.32	0.18
	Sap. Value	1.71	1.54
B.P. from 185 to 300°C	Yield	40.8	38.6
	Sp. Gr.	0.9042	0.9005
	n^{15}_{D}	1.4837	1.4829
	Acid Value	0.25	0.21
	Sap. Value	8.57	8.56
B.P. over 300°C	Sp. Gr.	0.9634	0.9662
	Acid Value	0.88	0.14
	Sap. Value	1.92	0.35
	Flash point		139
	Freezing point		below -10°C
	Viscosity Red. No. 1		100.8

Table X(B)2
PROPERTIES OF CHARGED OIL FOR CATALYTIC REFORMING

	Sample Oil	
	A	B
Origin	Terpene obtained by Stean dist.	Terpene obtained by carb.
Sp. Gr.(10/4)	0.865	0.865
Acid Value		1.18
n^{20}_{D}		1.461
I.D. (°C)	155	128
10 (%) (°C)	156.5	150.5
50 (%) (°C)	158	162
90 (%) (°C)	160	164
97 (%) (°C)	188	297
D.P. (°C)	220	322

ENCLOSURE (B)2

Table XI(B)2
YIELD OF PRODUCT AND PROPERTIES OF GASOLINE FRACTION OBTAINED

		Sample	
		A	B
Sample used, (cc)		1075	1000
Yield of Product	Oil (cc)	905	800
	Water (cc)	20	20
	Gas (l)	67.0	67.1
Distillation Properties of Gasoline Fraction	Sp. Gr.(15/4)	0.838	0.841
	I. D. (°C)	49.5	46.0
	10% (°C)	97.0	100.0
	50% (°C)	158.0	166.0
	90% (°C)	189	188.0
	97% (°C)	199	199
Octane Value	unleaded	87.2	89.0
	leaded 0.15%	93.6	94.0

Table XII(B)2
PROPERTIES OF AVIATION GASOLINE OBTAINED BY CATALYTIC HYDRO-CRACKING

Composition	Sp. Gr. (25/4)	0.7869
	Unsat. H.C.(%)	1.50
	Arom. H.C.(%)	3.15
	Naph. H.C.(%)	28.60
	Paraf. H.C.(%)	66.75
Distillation Property	I.D. °C	54
	10% °C	87
	50% °C	127
	90% °C	164
	97% °C	186
Octane Value	unleaded	74.4
	leaded 0.15%	94.8

ENCLOSURE (B)2

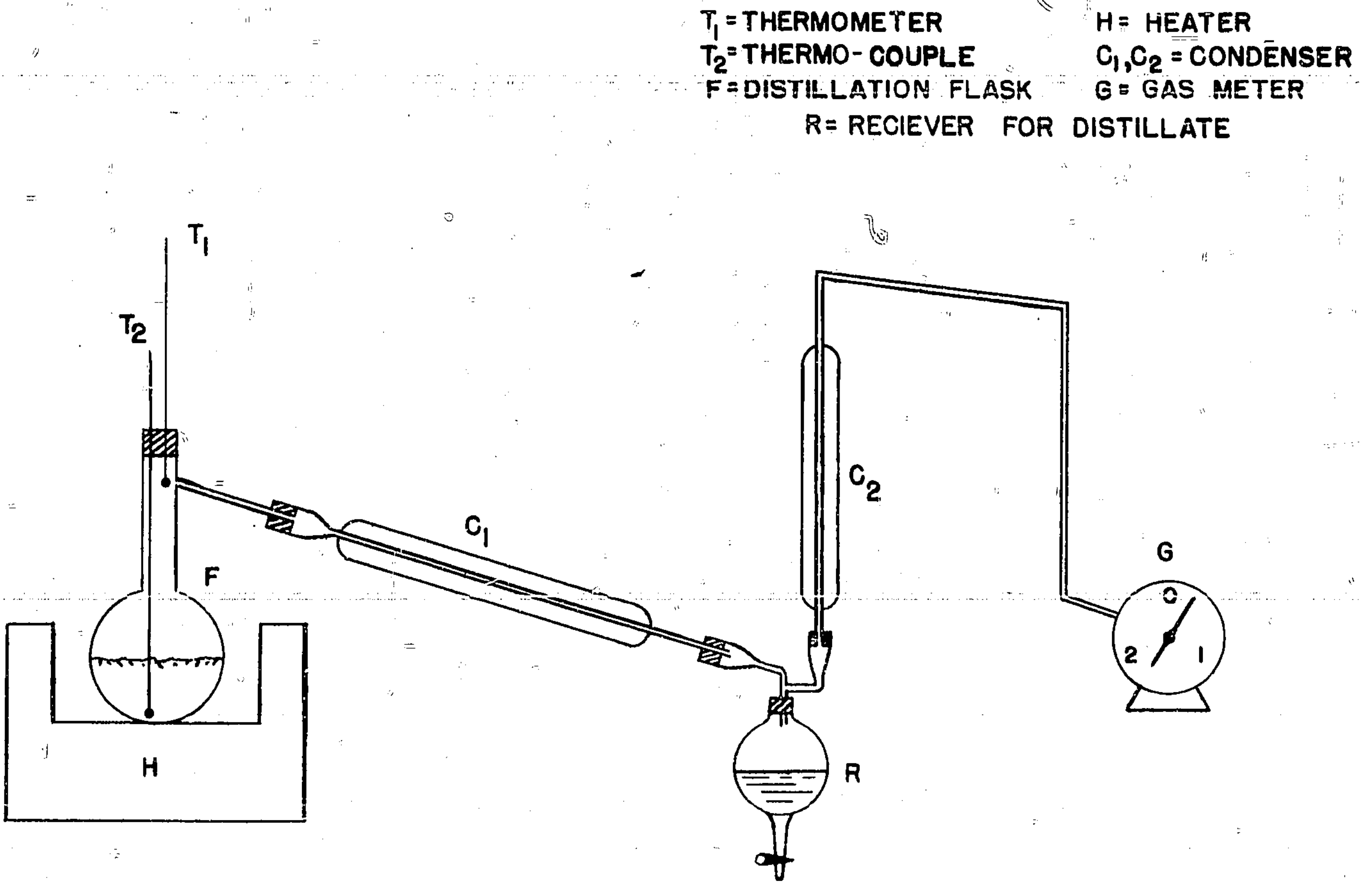


Figure 1(B)2
APPARATUS FOR THE CARBONIZATION OF PINE RESIN

ENCLOSURE (B) 3

STUDIES ON THE CATALYTIC REFORMING OF PINE ROOT OIL

by

CHEM. ENG. COMDR. H. FUJIMOTO

Research Period: 1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)3

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)3

SUMMARY

This research was projected to improve the stability of pine root oil for use in aviation engines. For this purpose the fraction boiling up to 185°C, namely the monoterpene parts of pine root oil, was reformed catalytically to a stable hydrocarbon mixture. The reaction proceeds as follows:

3 Monoterpene → 2 Cymene + 1 Menthane

It is carried out at a temperature of 350°C to 400°C and atmospheric pressure over activated Japanese acid clay catalyst. The reaction products were planned for use as aviation gasoline after blending with 40% of ethyl alcohol. The yields of reformed gasoline were about 65% of the charging stock.

I. INTRODUCTION

This research was done from January to April 1945, and the results were turned over to the Process Engineering Department for the development and design of a simplified commercial unit.

This research was carried out by Eng. Lt., M. MURAKAMI & Asist. Eng. M. MIYAZAKI.

II. DESCRIPTION

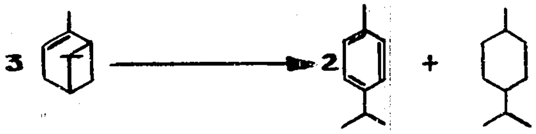
The test apparatus is shown in Figure 1(B)3. The fraction boiling up to 185°C obtained by the laboratory distillation of pine root oil was used as the charge stock. It was washed with 10% caustic soda solution to remove corrosive organic acids (butyric acid, C_5 acids, etc.) and esters. Tests with untreated oil indicated corrosion to test apparatus and also corrosive properties and dark color of the final aviation gasoline cut which could not be removed by final caustic treatment. Properties are shown below:

Sp. gr. (15/4)	0.859
Distillation test (°C)	
I.D.	150
10%	157
50%	170
90%	203
E.P.	265
Olefins (%)	89.2
Aromatics (%)	6.8
Naphthenes and Paraffins (%)	4.0
Octane Value Plain	70.6
Octane Value Leaded 0.15%	74.5
A.S.T.M. glass dish gum test	200mg/100cc

Five litres of charge stock were passed through the reaction tube containing 1 litre flash pelleted acid clay catalyst at a liquid space velocity of 1.0 and atmospheric pressure. Results are shown in Table I(B)3.

It was observed from this experiment that the monoterpene parts of pine root oil can be reformed to stable and high octane fuel which can be used for aviation. It is believed that the reaction proceeds according to the following equation.

ENCLOSURE (B)3



It was next tried to carry out this reaction using a simple apparatus, such as a batch-type still, which could be operated by farmers working on the dry distillation of pine roots in the country. For this purpose, the apparatus shown in Figure 2(B)3 was employed.

Five liters of stock similar to that used in the previous experiment were charged to the retort in each run. Properties were as follows:

Sp. gr. (15/4)	0.866
Distillation test (°C)	
I.D.	140
10%	158
50%	170
90%	226
E.P.	274

The distillation rate was held constant so as to distill the contents in 5 hours. The distillate was reformed in the reaction vessel and condensed to the receiver. Experimental results are shown in Table II(B)3.

The distillates were redistilled up to 185°C to obtain gasoline stock for aviation. The yields and properties of the products are shown in Table III(B)3.

These results were turned over to the Process Engineering Department to serve as the basis for the design of a simple commercial plant. A temperature of 350°C was selected for the commercial plants. Samples of the gasoline were tested at the First Naval Technical Center at YOKOSUKA. The gasoline by itself was not satisfactory due to low volatility. A blend with 40% by vol. of ethanol was found to be satisfactory for use in training planes.

ENCLOSURE (B)3

Table I(B)3
TEST RESULTS

Reaction	350°C	400°C	450°C	500°C
Yields of Gas (lit/lit of charge)	15.2	19.7	26.0	38.3
Yields of Gasoline Stock (Vol.% of charge)	77.6	71.8	66.6	56.0
Yields of Residue (Vol.% of charge)	7.2	8.5	7.4	5.7
Properties of Gasoline Stock				
Sp. gr. (15/4)	0.836	0.838	0.842	0.843
Distillation test (°C)				
I.D.	70	68	67	64
10%	126	120	115	117
50%	171	171	162	162
90%	187	190	191	186
E.P.	211	214	213	207
Olefines (%)	5.0	4.0	5.0	6.0
Aromatics (%)	70.4	73.7	72.0	79.5
Naphthenes (%)	10.2	8.6	23.0	4.8
Paraffins (%)	14.4	13.7		9.7
Octane Value, plain	83.3	88.5	89.4	89.9
Octane Value, leaded 0.15%	93.0	93.6	94.8	93.9
A.S.T.M. glass dish gum test, mg/100cc	0.8	3.4	2.6	1.2

ENCLOSURE (B)3

Table II(B)3
EXPERIMENTAL REFORMING RESULTS

Reaction temperature (°C)	300	350	400
Total distillate (Vol.% of charge)	86.0	83.9	77.7
Vol. of cracked gas (liter)	41.1	37.5	210.4
Properties of distillate Sp. gr. (15/4)	0.865	0.845	0.840
Distillation test (°C)			
I.D.	90	48	45
10%	162	144	124
50%	181	171	170
90%	336	279	264
E.P.	390	364	369

Table III(B)3
YIELDS AND PROPERTIES OF PRODUCTS ON REDISTILLATION

Yields of gasoline stock (Vol.% of charge)	61.8	62.5	61.4
Properties of gasoline stock Sp. gr. (15/4)	0.841	0.835	0.837
Distillation test (°C)			
I.D.	113	76	69
10%	152	136	122
50%	168	165	160
90%	178	181	179
E.P.	193	199	191
Olefines (%)	9.8	4.8	8.0
Aromatics (%)	51.7	61.2	68.6
Naphthenes (%)	28.5	11.5	12.8
Paraffins (%)	28.5	22.5	10.6
Octane Value leaded 0.15%	91.8	93.8	92.7
A.S.T.M. glass dish gum test, mg/100cc	3.8	3.6	3.3

ENCLOSURE (B)3

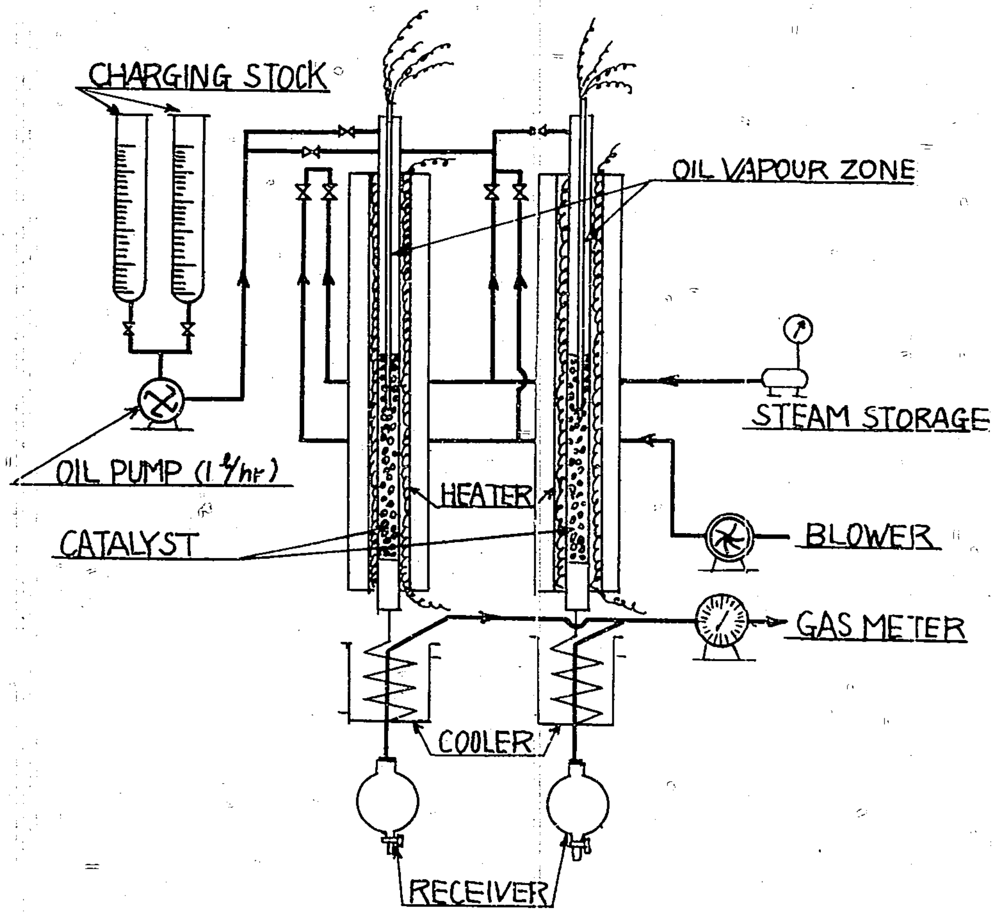


Figure 1(B)3
APPARATUS OF CATALYTIC REFORMING

ENCLOSURE (B)3

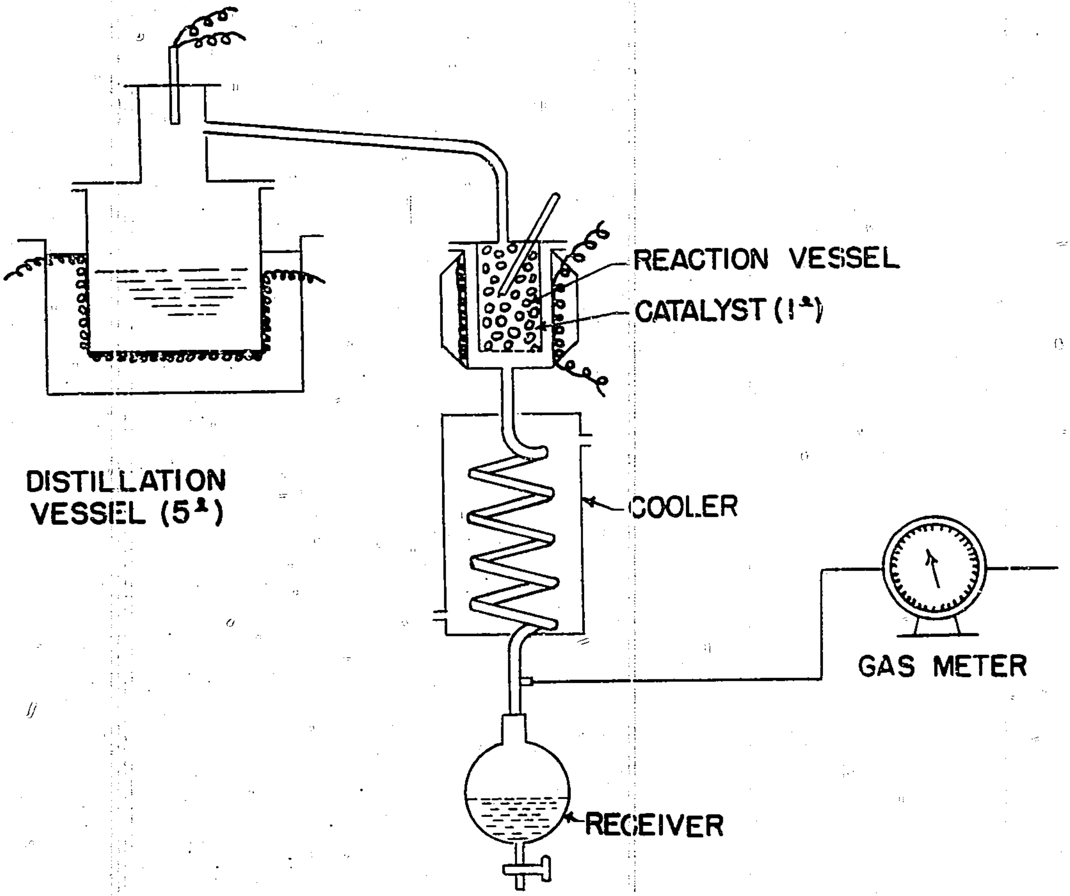


Figure 2(B)3
APPARATUS OF SIMPLIFIED CATALYTIC REFORMING

ENCLOSURE (B) 4

DESIGN STUDIES ON THE SIMPLIFIED TREATING PROCESS FOR PINE ROOT OIL

by

NAV. CHEM. ENG. LT. COMDR. S. SANKA

Research Period: 1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)4

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)4

SUMMARY

Design studies were made of a process to make aviation gasoline from pine root oil. This process has three steps. The 1st step is distilling and coking of pine root oil. The next is the catalytic reforming of the gasoline fraction. The 3rd step is redistillation of the reformed oil.

Batch type operation is employed for each step. Photographs and detailed blue-prints of each unit are attached.

I. INTRODUCTION

A. History

Carbonization retorts were already in operation in our country, but were widely scattered. In consequence, large central pine root oil refineries were not practical due to transportation difficulties, and design work was started on apparatus to refine the oil on the spot.

In April 1945, orders were given to study this project. Since reliable data was not available, we constructed a pilot plant based on common sense principles and chiefly studied how to operate this apparatus.

B. Key Research Personnel Working on Project

Nav. Eng.	T. SHIBAZAKI
Nav. Chem. Eng. Lt. Comdr.	S. SANKA
Nav. Chem. Eng. Lt.	T. YOKOYAMA
Nav. Chem. Eng. Lt.	T. UEDA
Nav. Chem. Eng. Lt.	R. SUSUKI
Nav. Chem. Eng. Lt.	Y. MOTOYAMA
Nav. Sub-Eng.	M. KUBOTA

II. DETAILED DESCRIPTION

A. Distilling and Coking Apparatus

1. Test Procedure. A diagram of the distilling and coking apparatus is shown in Plate I(B)4. In this apparatus crude pine root oil is fractionally distilled into light and heavy cuts. The volume of the batch still is 1.2 kl and the volume of pine root oil charged is 0.75 kl. The relation between yield of oil, temperature of retort, and time is given in Figure 2(B)4. It is necessary to control firing carefully in oil temperature range of 90°C to 110°C to avoid sudden foaming of oil due to occluded water. After water is distilled over, the firing rate is increased to approximately 20kg/hr of wood. When distillation of the oil is completed, the retort is allowed to cool for 2-3 hours until temperature of retort becomes less than 120°C.

The coke is removed from the bottom of the retort every 4 runs. When the crude pine root oil contains more than 7% of water, the required time per cycle becomes very long. Accordingly, when the crude oil has more than 7% of water, it is setted about 3.5 hours at 60-70°C. By this treatment, the water content is reduced to less than 4%.

The first cut is taken at 185°C still temperature and is used as feed for the catalytic reforming unit. It was planned to use the distillate above 185°C as feed for catalytic cracking.

2. Experimental Results. Experimental results are given in Table I(B)4.

B. Simplified Catalytic Reforming Apparatus

1. Test Procedure. A diagram of this apparatus is shown in Plate II(B)4. 0.5 Liters of the gasoline fraction (185°C end point) obtained from the "distilling and coking apparatus" is charged into a batch still, (1.2 kl Volume) and distilled by direct wood firing.

The oil vapors are passed through the reaction chambers, filled with activated Japanese clay catalyst. The reactinn conditions are about 450°C and atmospheric pressure.

After many experiments the operating curve of Figure 3(B)4 was obtained. This apparatus has two firing grates, one on the still pot side and the other on the reaction chamber side, as shown in Figure 3(B)4. The reaction chambers are fired first, until the catalyst temperature reaches about 200°C, then firing of the still pot is started. After about 2 hours the oil vapors pass downward through the two parallel reaction chambers in which temperature has increased to 300°C. The catalyst size is 6mm(diameter) X 6mm(length) and is random packed, 25kg in each chamber. When catalytic action begins, the temperature T_2 suddenly rises to 550-600°C. By controlling rate of firing and valve openings the temperature is regulated to 450°C.

The vaporization of oil is continued for 8 hours at the rate of about 60 lit/hr. If the firing rate on the evaporator side is too high, the oil flow is too great and the temperature of catalyst cannot be maintained at 450°C. The fire man must have experience to acquire the proper technique for maintaining a uniform reaction temperature. The final still pot temperature is about 230°C. The valves connecting catalyst and oil chamber are tnen closed. About 8 liters of water are added to each reactor, forming steam which blows down the lines. Catalyst temperature is about 300°C and air, at atmospheric temperature and pressure of 500mm Hg, is blown through the catalyst. The air blow is about 500m^3/hr for both retorts. If the blower capacity is less than this, not only is the steel shell of the reaction chamber often burnt out by the reaction heat, but the catalyst also loses activity. The air flow is continued for about 35 minutes and catalyst temperature increases to 650°C maximum. Eight liters of water are added again to decrease the temperature. This cycle is repeated 4 times (refer to Figure 3(B)4). After this, the temperature of catalyst increases gradually due to the natural flow of air. The still pot is allowed to cool, and when the temperature is 100°C fresh oil is charged. The fuel consumption on each side is about 12-15 kg/hr and the total fuel consumption in one cycle is about 300 kg of wood.

2. Experimental results are given in Table II(B)4.

C. Re-Distilling Apparatus

1. Test Procedure. A diagram of this process is given by Figure 1(B)4. This apparatus is used to refine the reformed oil from the catalytic reforming apparatus. The batch still itself is the same as in the simplified catalytic reforming unit. The distillation tower is packed with clay Raschig rings, 3- X 30mm in size.

This operation is very simple and is not reported. Oil is distilled at the rate of 75 lit/hr and the fuel consumption is 15 kg/hr.

2. Experimental Results. Experimental Results are given in Table III(B)4.

Table I(B)4
OPERATION AND PRODUCTS OF PINE ROOT STILL

	Fraction	Engler Distillation	Distillate from Pilot Retort
Yield of Product	Below 185°C	20% (Vol)	20% (Vol)
	185-300	28	25
	Above 300	42 (as residue)	30
	Cokes		5
	Water	3	5
	Gas and Loss	7	15

Operating Time .... 9.5 hr/run
Capacity of Still .... 0.75 kl/run
Fuel Consumption .... 180 kg(wood)/run
Operators Required .... 2 men
Discharge of Cokes .... one discharge/4 runs

ENCLOSURE (B)4

Table II(B)4
GASOLINE FROM CATALYTIC REFORMING

		Charge Oil	Reformate
Specific Gravity		0.86	0.85
Dist Temp. (°C)	1st Drop	110	70
	10%	140	135
	50%	170	165
	97%	190	200
	Dry Point	250	280
Octane Value	0% T.E.L.	70	85
	0.15% T.E.L.	75	90

Yield of Reformed Oil
- Reformed Oil .... 80% (vol)
- Gas and Loss 20%

Space Velocity of Oil .... 1 vol oil/vol cat/hr
Reaction Temperature .... 450°C

Operating Time
- Catalytic Reforming .... 8 hr
- Reactivation of Catalyst .... 3 hr
- Charge and Others .... 5 hr

Total .... 16 hr

Table III(B)4
REDISTILLATION OF REFORMED OIL

	Before Treatment	After Treatment
1st Drop	70°C	70°C
10%	135	130
50%	160	160
97%	200	190
Dry Point	280	250
Color	deep green	light brown

Operating Time .... 10 hr/run
New Charge .... 0.75 kl/batch
Yield of Oil
- Refined Oil .... 80% (vol)
- Residue 20%

Fuel Consumption .... 150 kg/run

ENCLOSURE (B)4

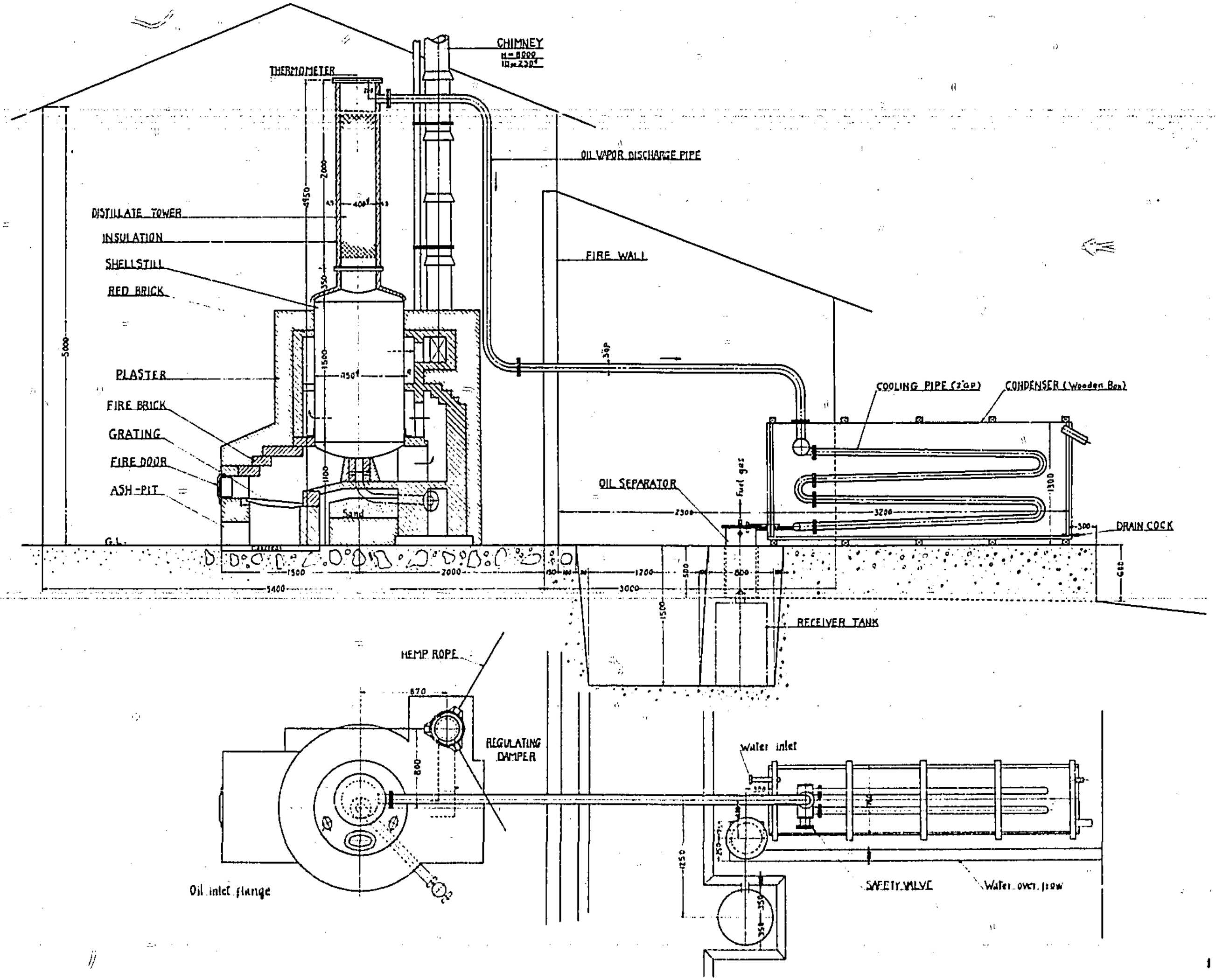


Figure 1(B)4
GENERAL ARRANGEMENT OF RE-DISTILLATION APPARATUS OF PINE-ROOT OIL
Daily Capacity 1.5 kl

ENCLOSURE (B)4

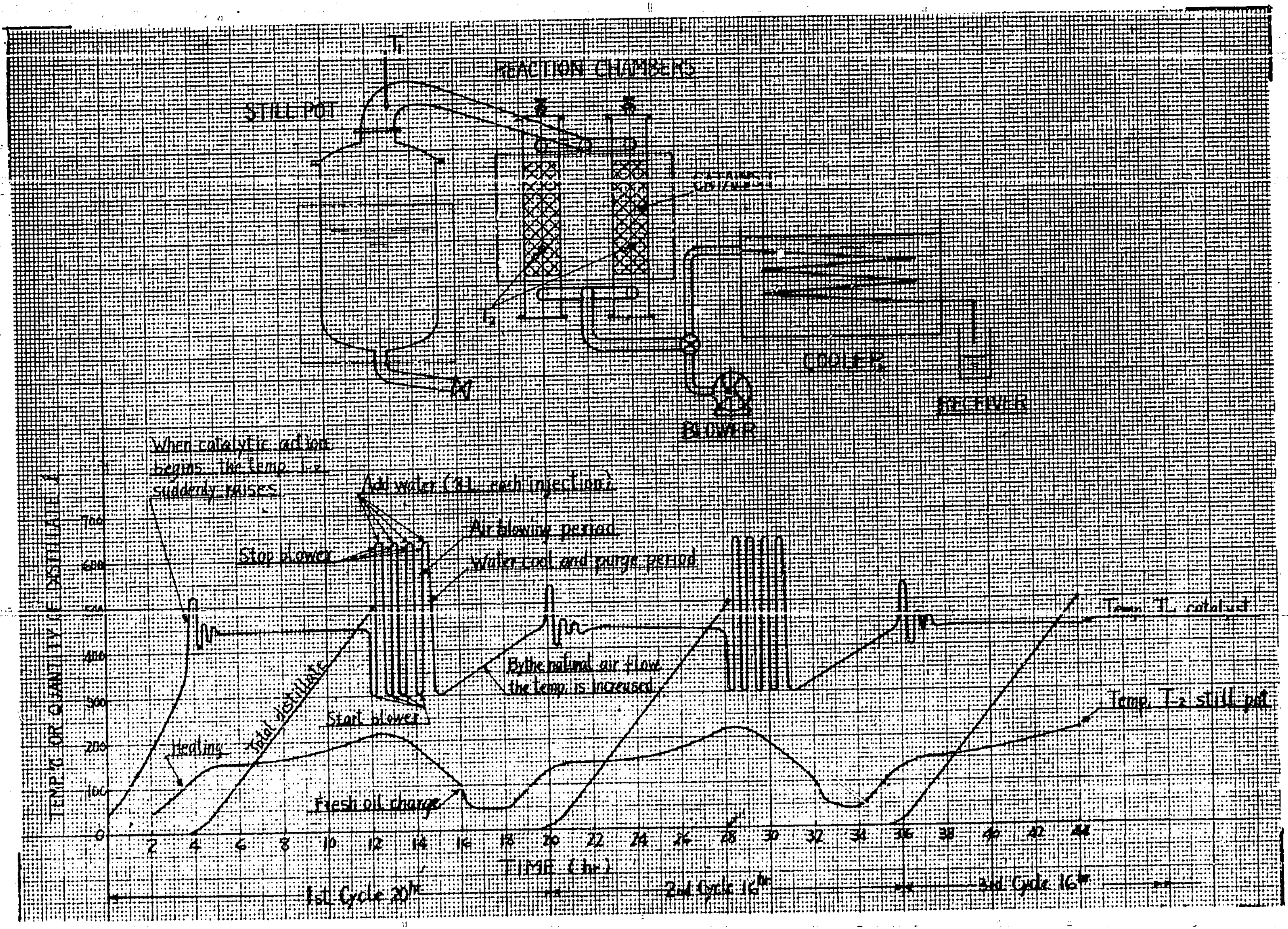


Figure 2(B)4

RELATION BETWEEN YIELD, TEMP. AND TIME FOR DISTILLATION OF CRUDE PINE ROOT OIL

ENCLOSURE (B)4

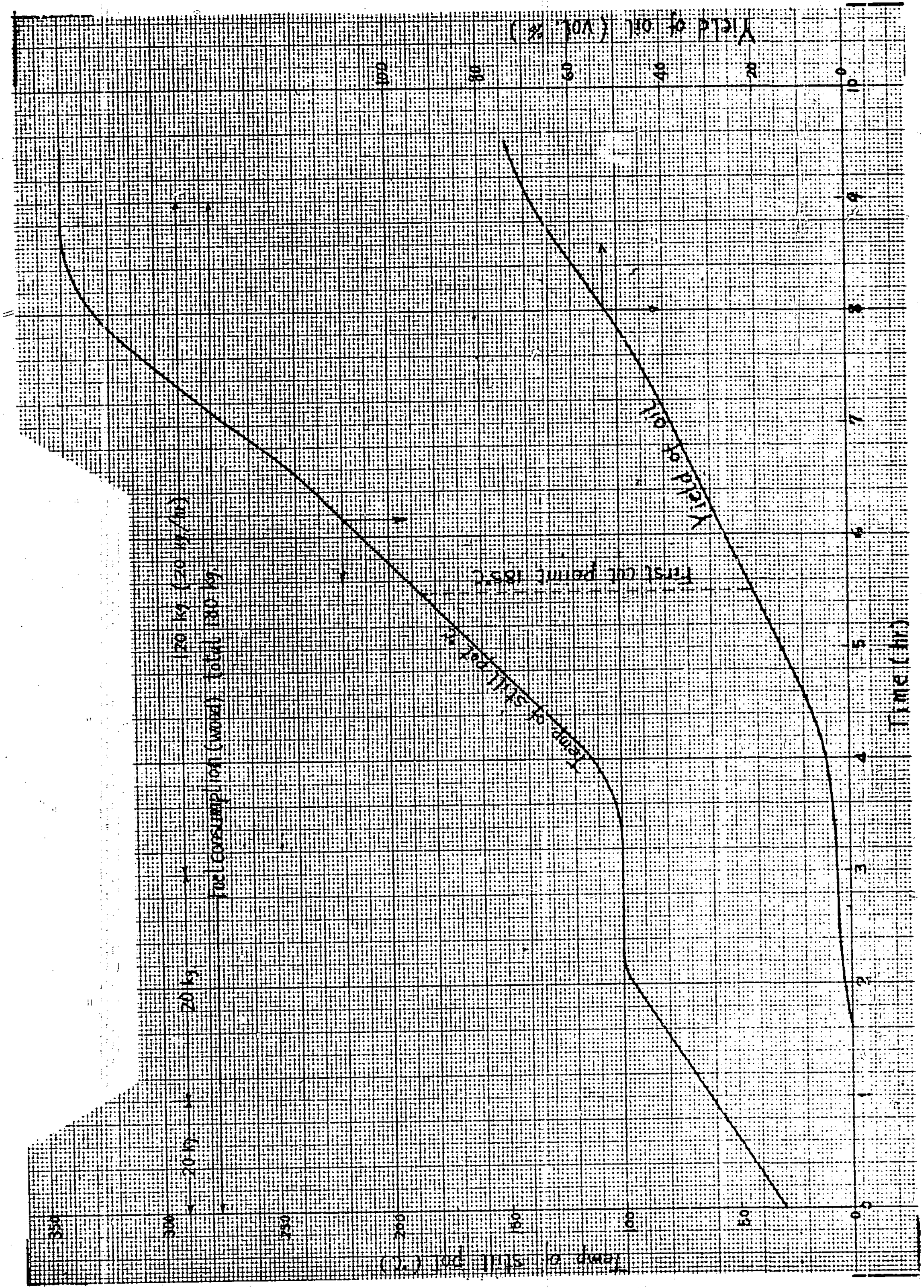


Figure 3(B)4
OPERATING CURVES ON CATALYTIC REFORMING UNIT

ENCLOSURE (B)4

Figure 4(B)4
SIMPLIFIED DISTILLATION
AND CARBONIZATION PLANT

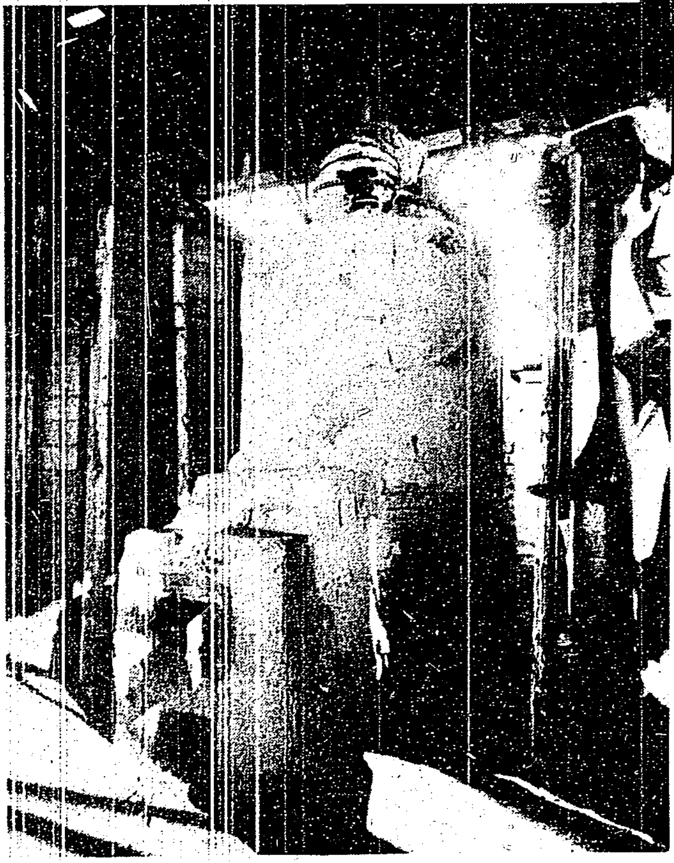


Figure 5(B)4
SIMPLIFIED CATALYTIC REFORMING
OF PINE-ROOT OIL

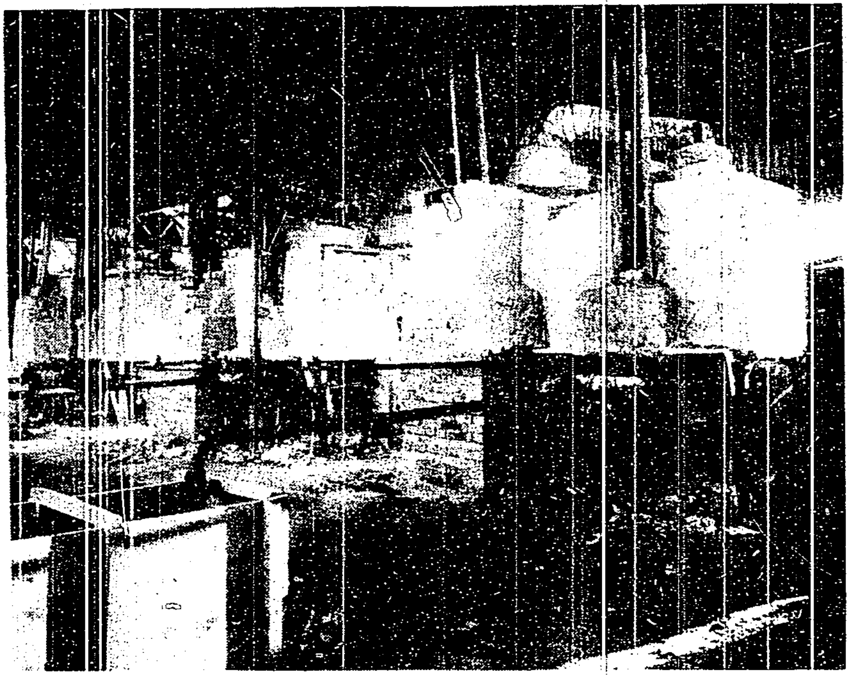
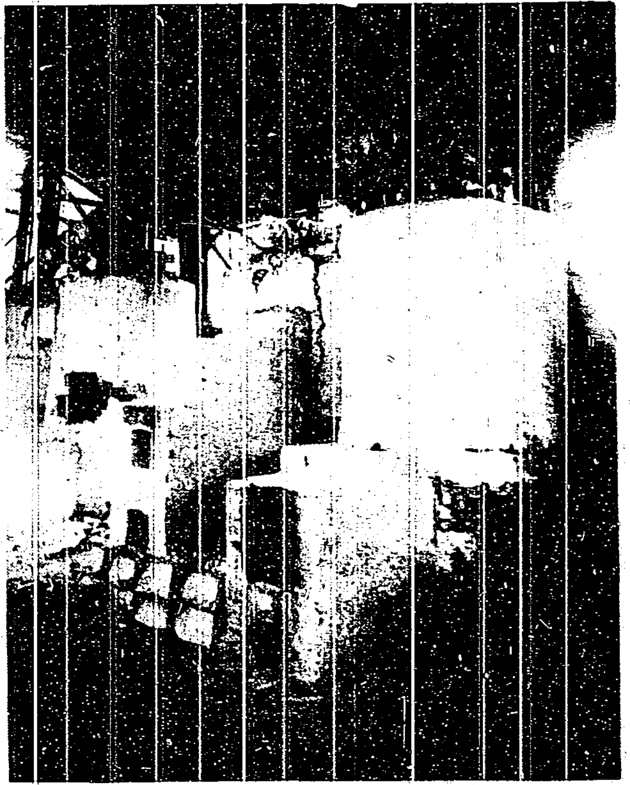


Figure 6(B)4
SIMPLIFIED CATALYTIC REFORMING
OF PINE-ROOT OIL

Figure (B)4
SIMPLIFIED CATALYTIC
REFORMING PLANT



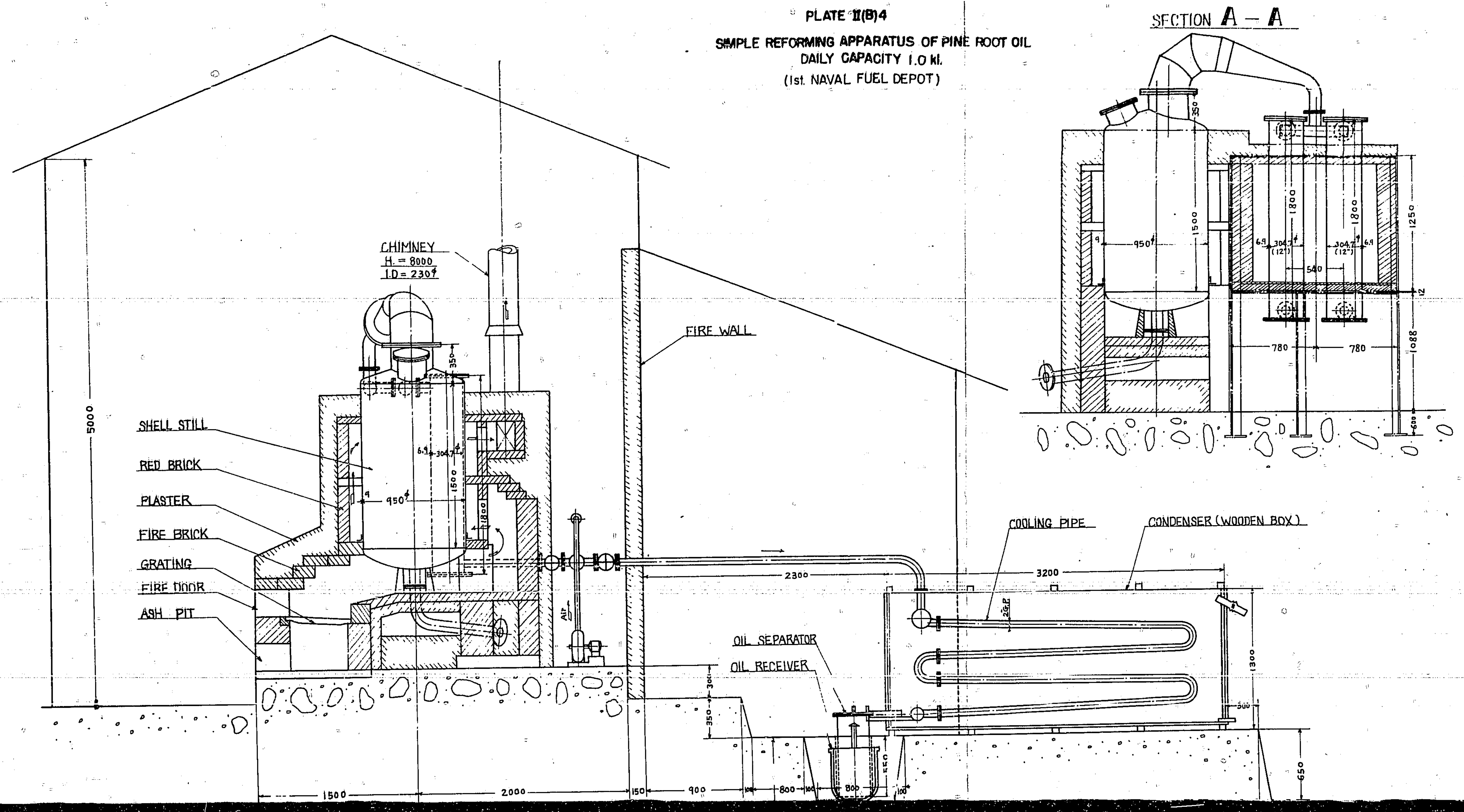
ENCLOSURE (B)4

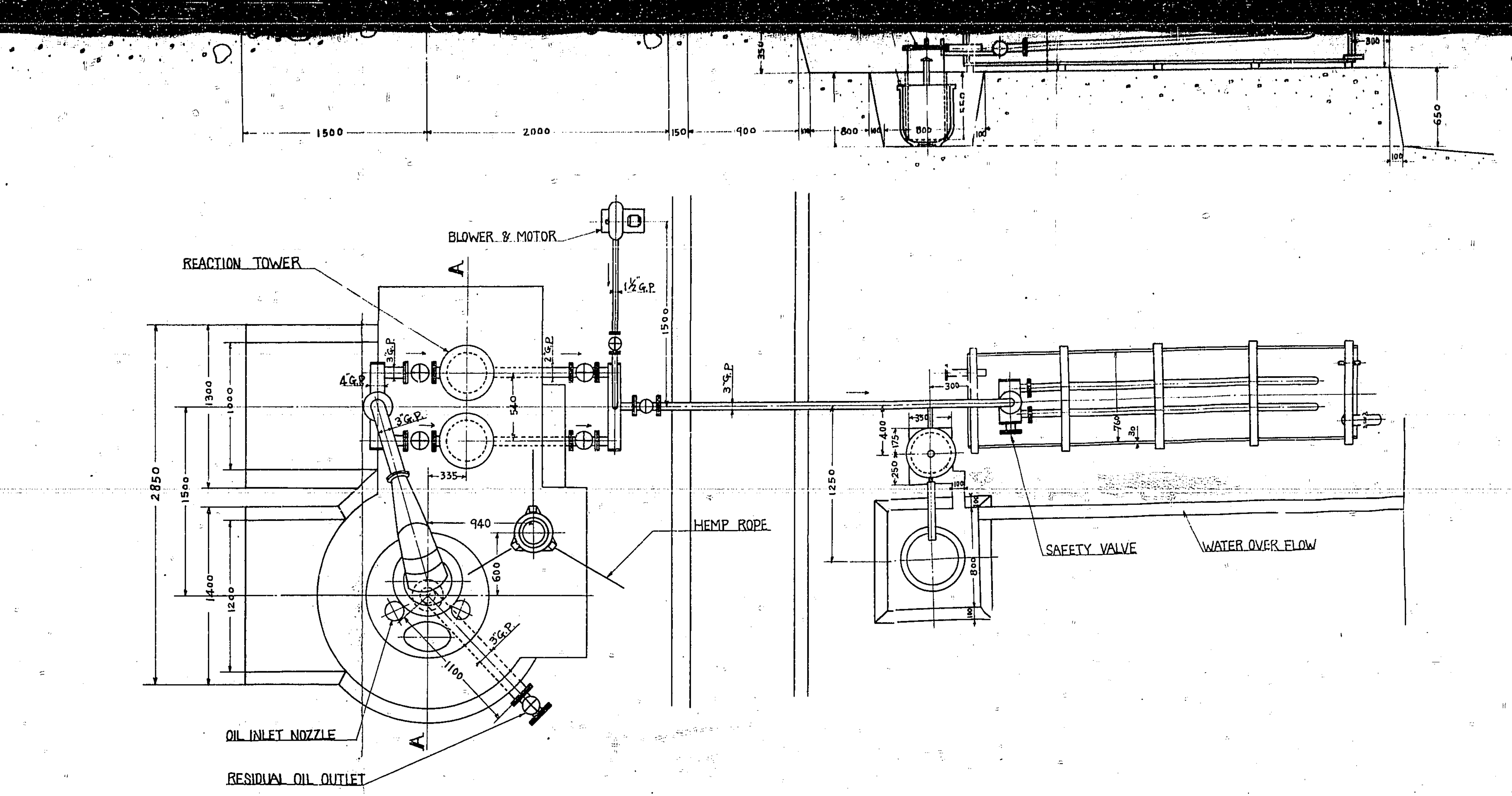
Figure 8(B)4
SIMPLIFIED REDISTILLATION PLANT

Figure 9(B)4
SIMPLIFIED REDISTILLATION PLANT

PLATE II(B)4

SIMPLE REFORMING APPARATUS OF PINE ROOT OIL
DAILY CAPACITY 1.0 kl.
(1st NAVAL FUEL DEPOT)





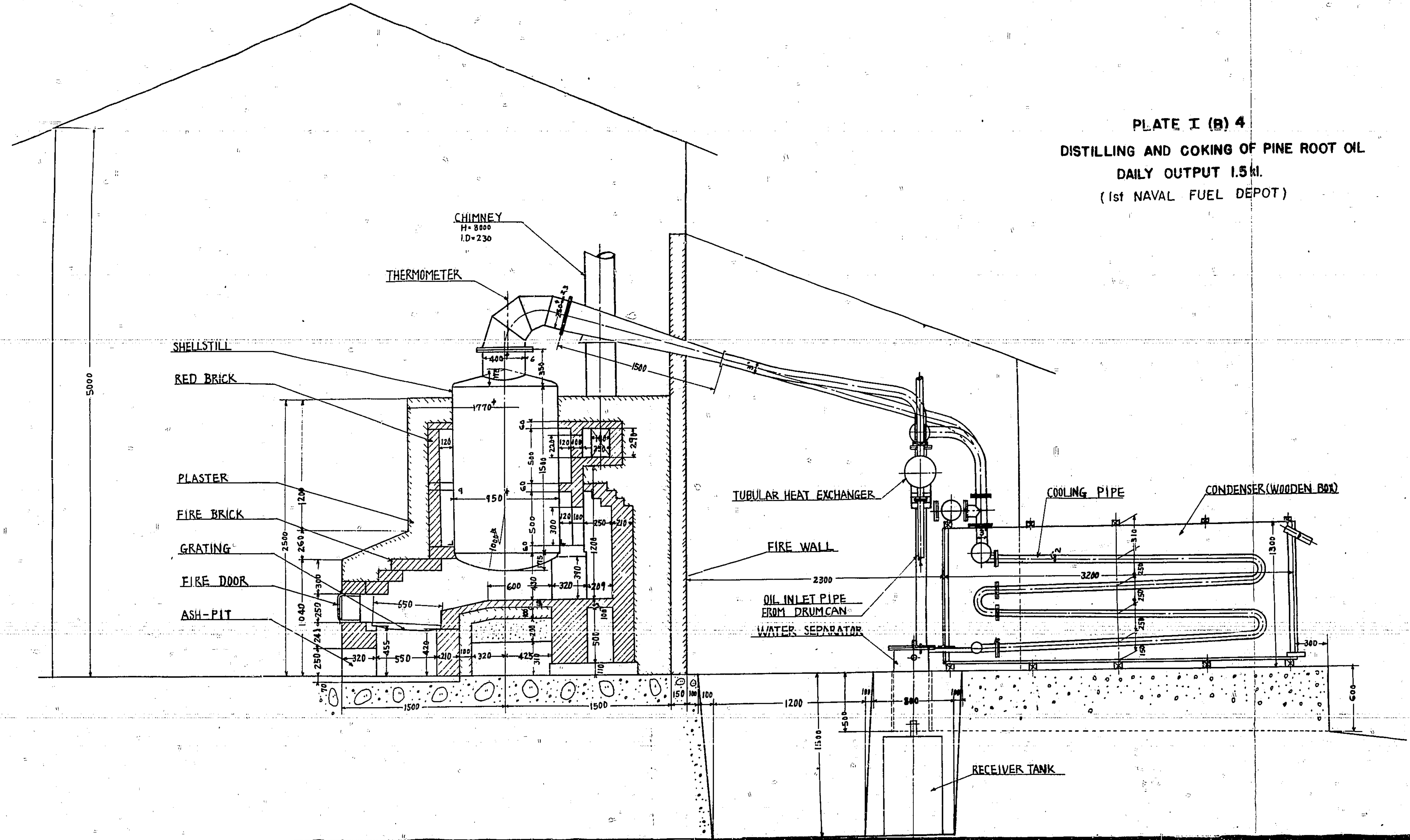
REACTION TOWER
BLOWER & MOTOR
1½" G.P
1500
4" G.P
3" G.P
2" G.P
3" G.P
3" G.P
3" G.P
A
A
2850
1300
1600
1500
1400
1200
540
335
940
600
1100
HEMP ROPE
OIL INLET NOZZLE
RESIDUAL OIL OUTLET
300
350
400
175
250
1250
760
30
100
800
SAFETY VALVE
WATER OVER FLOW
1500
2000
150
900
800
650
350

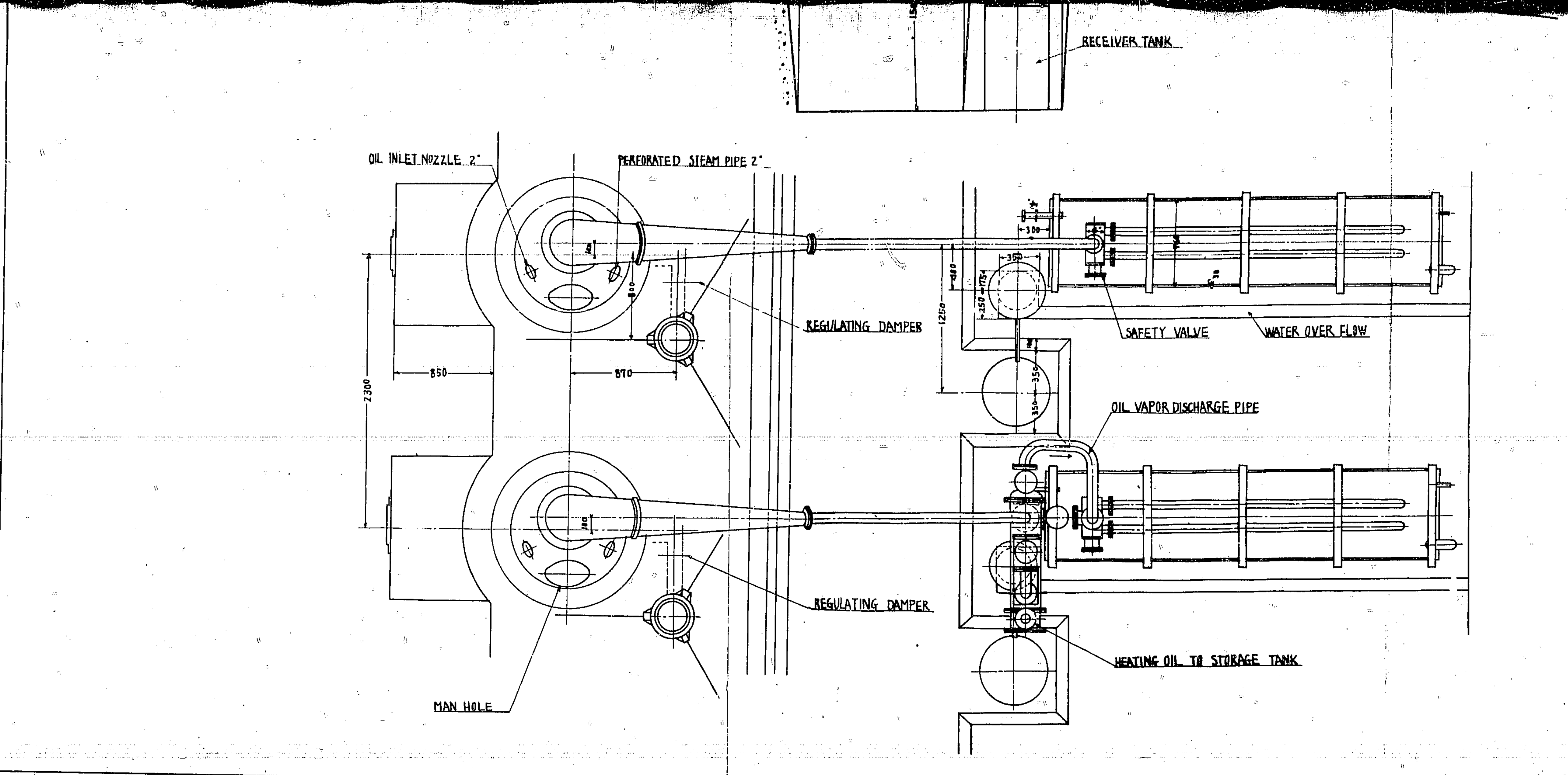
PLATE I (B) 4

DISTILLING AND COKING OF PINE ROOT OIL

DAILY OUTPUT 1.5 kl.

(1st NAVAL FUEL DEPOT)




RECEIVER TANK
OIL INLET NOZZLE 2"
PERFORATED STEAM PIPE 2"
REGULATING DAMPER
SAFETY VALVE
WATER OVER FLOW
OIL VAPOR DISCHARGE PIPE
REGULATING DAMPER
HEATING OIL TO STORAGE TANK
MAN HOLE
850
870
2300
800
300
350
1250
250
350
350

ENCLOSURE (B) 5

PILOT PLANT CATALYTIC CRACKING STUDIES ON SUMATRA KEROSENE AND PINE ROOT OIL

by

CHEM. ENG. COMDR.
H. FUJIMOTO

Research Period: 1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)5

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)5

SUMMARY

Pilot plant catalytic cracking experiments were carried out to produce aviation gasoline from Sumatra kerosene and from pine root oil fractions. Yields of aviation gasoline distillate were as follows:

Charging Stock	Yields
Sumatra Kerosene	25% by vol.
185° end point pine root distillate	70% by vol.
250° end point pine root distillate	50% by vol.
350° end point pine root distillate	35% by vol.

I. INTRODUCTION

The pilot plant, based on a U.O.P. catalytic cracking design, was completed in September 1943. Cracking tests on kerosene fractions from East Indies crudes were carried on until August 1944 by Chem. Eng. Lt., T. KOTANI. In this period several kinds of Japanese acid clays and U.O.P. synthetic catalyst were tested. The U.O.P. catalyst was manufactured by Nippon Gasoline Co. and was thought to be composed of aluminium silicate with zirconium oxide. The U.O.P. catalyst gave slightly higher octane number (about one unit) but was inferior to Japanese natural clays on basis of lower yields, higher olefine content of product, and higher cost of catalyst. The best catalyst was found to be acid clay from near KOMATSU City.

Starting in January of this year, tests on various fractions of pine root oil were carried out by Chem. Eng. Lt. Y. YAMASAKI.

II. DETAILED DESCRIPTION

A detailed flow chart of the pilot plant and operating conditions are shown on Figure 2(B)5. Catalyst used for these experiments was activated. Japanese acid clay produced near KOMATSU City, ISHIKAWA district. Physical and chemical properties of feed stocks and detailed experimental results are shown in Tables I(B)5, II(B)5, III(B)5, and IV(B)5.

The several feed stocks were as follows:

a) Sumatra light oil; Shipped from YOKKAICHI, Second Fuel Depot.
b) Pine root oil (-250°C), Distilled at OFUNA, column overhead.
c) Pine root (Heavy), Distilled at OFUNA, side cut.
d) Pine root oil (-185°C), Shipped from YOKUYAMA, Third Naval Fuel Depot.
e) Mixed light oil, Mixture of light oils of petroleum origin.
f) Pine root oil (L.O. fraction), Distilled in batch-type still at TSURUMI, Nippon Petroleum Co.

III. CONCLUSION:

On the basis of the above experimental results, it was planned to treat pine root oil commercially according to the scheme outlined in Figure 1(B)5.

In the above scheme catalytic reforming would be carried out in simple units located near the pine root retorts. The catalytic cracking would be carried out in larger more complex units at central refineries. If sufficient catalytic cracking capacity and transportation facilities were available, it would be more desirable catalytically to crack the two fractions separately under optimum conditions for each fraction, to produce satisfactory gasoline with the required volatility. Two catalytic cracking plants for processing kerosene from natural crude have been installed in Japan (at YOKKAICHI, the Second Naval Fuel Depot). Capacity of each plant was 2000 barrels/ day. Process designs were prepared at OFUNA on basis of pilot plant experiments.

It was planned catalytically to **crack pine** root oil at YOKKAICHI, but this was not accomplished by the end of the war. Some unsuccessful test runs were made on a catalytic unit at TSURUMI. It was also planned to construct some 21 catalytic cracking units, treating 10,20 or 30 kl of charge per day, to handle pine root oil in Japan, out no unit was completed.

Engine and flight tests were made on 40 kl of final catalytic cracked aviation gasoline plus 0.15% lead. Laboratory engine tests at the First Naval Technical Depot showed satisfactory results except for tendency to swell rubber connections. This problem was solved by substituting a better quality rubber. Flight tests in flighter planes made by YOKOSUKA Air Corps showed satisfactory results.

Table I(B)5
DISTILLATION OF CHARGING STOCKS

	Sumatra Light Oil	Pine Root Oil (~250°C)*	(~185°C)**	(Heavy Fract.)
Sp. Gr.	0.822	0.809	0.796	0.896
1st drop°C	81.5	65.0	72.0	122.0
10%	168.0	96.5	100.0	160.5
20%	182.5	110.5	112.0	170.5
30%	192.0	137.5	120.0	180.0
40%	202.5	146.0	128.0	189.0
50%	212.0	157.5	136.0	200.0
60%	223.0	162.0	145.0	217.0
70%	236.5	171.5	152.5	241.0
80%	251.0	181.5	159.0	272.0
90%	271.5	209.0	166.0	348.0
95%		222.0	172.0	
97%			175.5	
E.P.	331.0	238.0	179.5	
A.V.		0.30	0.20	0.60

*Washing of 1% alkali
**Distillation cut~185°C

ENCLOSURE (B)5

Table II(B)5
CHARACTERISTICS OF FEED STOCKS

		1	2	Prel.	3	4	5	6	7	8
Date		3.16 0900 3.17 0900	3.17 0900 3.18 0900	3.18 2100 3.19 0900	3.19 1600 3.20 0900	3.20 0900 3.21 0900	3.21 0900 3.22 0900	3.22 0900 3.22 2300	3.23 0900 3.24 0900	3.24 1200 3.25 0500
Run Period (hr)		24	24	12	17	24	24	14	24	17
Charging Stocks		Sumatra L. O.		Pine Root oil (-250°C Cut)			Pine Root oil (185°C Cut)			Pine root oil (Heavy)
Total Charge (lit)		3560	3540	1550	2810	3110	3290	2120	3380	2850
Charge per hour (lit/hr)		148	148	129	165	130	137	152	141	166
S. V.		5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Recycle ratio		6.6	6.6	7.6	5.9	7.5	7.1	6.4	6.9	5.9
Reaction Temp (°C)	Ist Reaction Chamb.	449	448	461	454	453	458	448	458	457
	2nd Reaction Chamb.	424	429	436	444	439	441	433	443	455
	3rd Reaction Chamb.	447	437	449	454	452	457	450	460	472
	Mean (°C)	440	438	443	451	448	452	444	454	461
Reaction Press (kg/cm^2)		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Oil Temp. Outlet of furnace tube (°C)		490	483	467	466	470	435	489	481	476
Oil Temp. Inlet of Reaction Vessel (°C)		485	480	459	458	462	477	482	471	476
Flue gas	Amount (m^3/hr)	865	865	865	865	865	855	865	865	865
	Heating Temp. (°C)	547	546	536	546	540	550	556	552	552
	Outlet of furnace tube (°C)	511	507	503	511	515	527	531	523	529
	Pressure (kg/cm^2)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Steam Temp. (°C)		242	286	285	281	278	265	265	274	274
Charging Stock Including Recycle	Sp. Gr. (15°/4°C)	0.857	0.850	0.855	0.856	0.848	0.831	0.831	0.842	0.841
	Ist Drop (°C)	87.5	89.0	72.0	104.0	74.5	84.5	84.5	104.0	82.0
	10 % (°C)	102.0	101.0	165.0	164.0	172.0	177.5	177.5	164.5	174.0
	50 % (°C)	202.0	196.0	213.0	212.5	229.5	223.0	223.0	212.5	224.0
	90 % (°C)	291.0	286.5	295.0	312.0	320.0	290.0	290.0	284.0	294.0
	E. P. (°C)	340.0	329.0	337.0	347.5	356.0	324.5	324.5	317.0	326.0
	U.O.P. Characterization	11.1	11.0	11.2	11.2	11.4	11.3	11.3	11.3	11.4
Flue gas	H_2S %									
	CO_2 %	8.5	7.8	8.7	9.1	8.8	8.7	7.5	9.2	9.3
	O_2 %	6.8	7.6	5.1	6.7	5.8	6.2	8.5	6.5	6.4
	CO %	2.4	2.0	3.9	1.4	2.7	2.2	1.1	1.8	2.1
Yields	Stabilised gas + Pentane (Vol%)	2.6	4.4	9.8	8.5	6.2	6.3	3.5	5.0	4.1
	Aviation Gas (Vol%)	25.0	25.0	73.6	70.3	73.4	70.7	38.8	69.4	34.7
	Naphtha (Vol%)									
	Kerosene (Vol%)	53.6	55.6		1.4	2.3	30.6	21.2		61.6
	Cracked Gas (wt%)	6.7	6.3	19.6	10.3	8.2	9.1	8.7	8.1	7.6
	Carbon (wt%)	6.2	6.3	9.7	6.9	8.6	8.6	6.6	8.2	6.0

ENCLOSURE (B)5

TABLE II(B)5 cont.
CHARACTERISTICS OF FEED STOCKS

		Run No.	1	2	Prel.	3	4	5	6	7	8	Sum	
Properties of Aviation Gasoline	Sp. Gr. (d15°/4°C)		0.752	0.754	0.757	0.769	0.762	0.762	0.765	0.774	0.783	0.761	
	Engler Dist	Ist drop (°C)	36.5	39.0	50.0	50.0	46.0	44.0	44.5	54.0	43.0	34.0	
		10 % (°C)	71.5	71.0	86.5	88.0	86.0	77.0	80.0	93.0	82.5	75.0	
		50 % (°C)	113.0	114.5	113.5	112.5	115.0	105.0	104.5	114.5	110.5	111.5	
		90 % (°C)	143.5	140.5	138.0	138.5	142.5	128.5	128.0	137.0	131.0	142.0	
		E. P. (°C)	175.0	169.0	174.5	165.5	176.5	172.0	167.5	173.5	170.0	178.0	
	Octane Value	Plain	75.6	79.0	74.6	74.6	75.0	75.2	77.0	74.8	80.3	75.6	
		Leaded 0.15%	92.7	92.5	90.6	91.0	90.3	90.3	92.2	92.5	93.4	91.7	
	Comp	Unsat (%)	9.0	11.0	9.0	10.5	10.5	11.0	14.0	9.0	17.0	10.0	
		Aromatic (%)	20.9	25.8	30.9	31.3	31.3	32.0	31.0	33.7	41.5	32.4	
		Naphthone (%)	24.3	19.8	22.2	21.3	21.3	20.9	20.5	21.0	14.4	1.1	
		Paraffin (%)	45.6	43.4	37.9	36.9	36.9	36.1	34.5	36.3	27.1	36.5	
	Read. Vap. Press (kg/cm²)		04.9	04.9	0.39	0.30	0.33	0.36	0.39	0.26	0.38	0.60	
Prop. of Recycle Stocks	Sp. Gr. (d15°/4°C)		0.832	0.831	0.842	0.849	0.846	0.856	0.869	0.867	0.896		Stabilized Gas
	Engler Dist	Ist drop (°C)	83.0	126.0	161.5	162.5	158.0	160.0	156.5	139.0	165.0		
		10 % (°C)	181.0	174.0	184.0	178.0	177.0	176.5	175.	154.0	172.0		
		50 % (°C)	216.0	226.0	211.5	203.0	199.0	200.0	207.0	192.0	199.0		
		90 % (°C)	222.0	263.5	271.5	265.0	259.0	262.0	282.0	277.5	294.0		
		E. P. (°C)	296.0	295.0	310.5	312.0	293.0	294.0	329.5	355.5	355.0		
	U.O.P. Characterization		11.4	11.6	11.3	11.2	11.3	11.1	11.1	10.9	10.8		
Gas Analysis	Sp. Gr. (Air = 1.0)		1.13	1.08	1.05	1.05	1.07	1.07	1.13	1.10	1.09		
	H_2 (%)							11.0		7.7	7.4	10.5	
	CH_4 (%)							30.2		32.8	34.0	30.4	
	C_2H_4 (%)							12.7		20.5	13.6	10.2	
	C_2H_6 (%)							2.9		6.8	4.6	12.2	3.1
	C_3H_6							16.0		9.4	16.7	7.2	31.4
	C_3H_8							2.0		6.4	6.1	9.3	17.0
	C_4H_8							5.0		3.4	2.0	2.1	7.8
	C_4H_{10}							2.3		0.6	3.7	3.7	3.7
	Above C_5							10.3		8.9	5.9	5.4	37.5
	O_2							0.5		0.4	0.6	0.2	
	CO							3.9		1.4	3.3	3.1	
	CO_2							2.3			2.0	2.0	
	N_2							1.9			2.3	3.7	

ENCLOSURE (B)5

Table III(B)5
DISTILLATION OF CHARGING STOCKS

	Mixed Light Oil	Pine Root Oil (L.O. Tract.)
Sp. Gr.	0.820	0.854
1st. drop°C	120.1	122.8
10%	123.5	150.0
20%	175.5	156.0
30%	187.5	163.5
40%	196.5	171.5
50%	207.5	177.5
60%	220.0	185.0
70%	233.5	.195.5
80%	249.5	214.5
90%	269.5	245.5
95%	285.0	266.0
97%	295.0	
E.P.	296.0	268.0
Acid Value		0.6
Alkali Value		6.

Table IV(B)5
CHARACTERISTICS OF PINE ROOT OIL FEED STOCKS

		1	2	Prel	3	4	5	6	7	8(I)	8(II)	9
Run No.		1	2	Prel	3	4	5	6	7	8(I)	8(II)	9
Dato		4.25 0900 4.26 0900	4.27 1300 4.28 1000	4.28 2100 4.29 0900	4.29 0900 4.30 0900	4.30 0900 4.30 2400	5.1 1600 5.2 1300	5.4 0900 5.5 0900	5.5 0900 5.6 0900	5.6 1200 5.6 2000	5.6 2000 5.7 0400	5.7 0900 5.8 1000
Run Period (hr)		24	21	12	24	15	21	24	24	8	8	25
Charging Stocks		Mixed light oil		Pine Root Oil (Light oil fraction)								
Total Charge (lit)		3400	2950	1560	3550	1730	3130	3450	2800	1050	950	3170
Charge per hour (lit/hr)		142	140	130	148	115	150	144	117	131	119	127
S. V.		5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
R. R.		5.9	6.0	6.5	5.6	7.5	5.5	5.7	7.3	6.4	7.1	6.7
Reaction Temp (°C)	1st Reaction Chamb	445	455	457	460	459	456	425	415	395	375	332
	2nd Reaction Chamb	440	445	455	657	455	452	425	420	400	380	316
	3rd Reaction Chamb	445	440	445	455	455	460	435	417	395	375	328
	Mean	443	447	452	457	456	456	428	417	397	377	325
Reaction Press (kg/cm^2)		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Oil Temp. Outlet of furnace tube (°C)		480	484	470	455	447	444	493	495	505	520	550
Oil Temp. Inlet of Reaction Vessel (°C)		447	468	448	447	428	424	468	467	674	500	505
Flue gas	Amounts (m^3/hr)	850	850	850	850	850	850	850	850	850	850	850
	Heating Temp. (°C)	549	545	541	537	504	539	426	390	286	166	68
	Outlet of furnace tube (°C)	513	516	510	508	483	816	407	375	280	164	67
	Pressure (kg/cm^2)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Steam Temp. (°C)		202	233	234	242	258	237	190	168	166	157	156
Charging Stock Including Recycle	Sp. Gr. (15°/4°C)	0.854	0.855	0.856	0.858	0.855	0.855	0.852	0.856	0.862	0.862	0.867
	1st drop (°C)	121.6	127.8	145.0	115.0	139.3	135.0	158.0	155.0	156.0	156.0	156.0
	10 % (°C)	160.0	161.5	165.0	167.0	168.0	168.0	172.0	173.0	175.0	175.0	173.0
	50 % (°C)	198.5	197.5	199.0	201.0	205.0	205.0	200.5	203.0	206.5	206.5	202.0
	90 % (°C)	284.0	282.5	287.5	282.0	289.0	286.5	281.0	285.0	285.0	285.0	289.0
Flue gas	CO_2 %	8.5	8.8	9.2	8.0	8.9	9.6	Air only				
	O_2 %	6.4	7.1	6.5	6.5	6.4	7.9					
	CO %	1.6	1.3	1.3	1.6	1.6	1.2					
Yields	Stabilized Gas + Pentane (Vol%)	4.3	2.8	5.2	4.2	4.5	3.8	2.6	4.1	3.3	5.1	5.0
	Aviation Gas (Vol%)	29.1	16.9	46.2	42.6	58.5	54.5	49.0	47.7	39.1	45.7	45.0
	Naphtha (Vol%)	40.3	62.0	35.2	21.1	22.6	21.7	37.7	20.7	21.0	17.9	28.4
	Cracked Gas (wt%)	8.5	8.8	16.0	13.6	15.5	14.8	15.1	17.9	17.1	18.9	17.4
	Carbon (wt%)	6.7	6.1	6.6	7.6	9.9	6.8					

Table IV(B)5 (Cont.)
CHARACTERISTICS OF PINE ROOT OIL FEED STOCKS

		Run No.	1	2	Prel.	3	4	5	6	7	8(I)	8(II)	9	Sum
Properties of Aviation Gasoline	Sp. Gr. (d15°/4°C)		0.761	0.746	0.784	0.793	0.799	0.798	0.791	0.797	0.799	0.796	0.782	0.786
	Engler Dist	1st drop (°C)	45.5	41.5	46.0	48.5	50.0	50.0	47.0	46.5	49.5	47.5	43.5	45.5
		10 % (°C)	75.5	62.0	82.5	87.0	88.0	89.5	84.5	87.5	89.5	87.0	78.0	76.0
		50 % (°C)	111.0	95.5	111.5	117.0	116.5	120.0	112.5	117.5	120.8	115.0	112.0	115.0
		90 % (°C)	134.0	125.0	147.0	144.0	143.0	154.0	138.5	144.5	146.5	140.0	133.0	149.0
		E. P. (°C)	165.5	150.0	159.0	168.0	161.5	176.5	162.0	162.0	166.0	164.5	168.0	167.5
	O.V.	Plain	79.2	80.0	81.2	80.9	82.0	81.0	81.6	82.6	82.4	82.2	81.3	81.7
		Leaded 0.15%	91.5	91.8	90.5	90.5	91.0	89.6	91.2	91.0	90.8	90.5	88.0	91.2
	Comp	Unsat (%)	10.0	20.5	21.5	19.8	22.0	19.5	19.5	21.0	19.5	22.5	16.5	19.5
		Aromatic (%)	30.6	22.3	25.9	37.8	40.6	39.5	39.4	41.8	40.9	40.6	30.5	40.1
		Naphthene (%)	23.2	27.6	27.9	12.2	19.2	20.6	17.9	13.4	22.1	15.9	18.2	19.0
		Paraffin (%)	36.2	29.6	24.7	30.5	18.2	20.4	23.2	23.8	17.5	21.0	36.8	20.2
	Read Vap. Press (Kg/cm^2)		0.47	0.58	0.37	0.32	0.32	0.47	0.38	0.32	0.29	0.31	0.41	0.60
Prop. of Recycle Stocks	Sp. Gr. (d15°/4°C)		0.841	0.845	0.847	0.873	0.877	0.871	0.890	0.897	0.886	0.886	0.901	
	Engler Dist	1st drop (°C)	157.0	160.5	170.0	144.5	169.5	166.0	181.0	175.5	169.0	169.0	171.0	
		10 % (°C)	180.5	180.5	185.0	179.0	181.0	189.0	205.5	198.0	183.5	183.5	184.5	
		50 % (°C)	208.5	211.0	218.5	209.5	210.0	221.0	249.5	233.0	214.5	214.5	224.0	
		90 % (°C)	267.0	266.0	272.5	285.0	294.0	292.5	333.0	300.5	288.5	288.5	306.0	
		E.P.				344.5								
Gas Analysis	Sp. Gr. (Air = 1.0)		1.13	1.15	1.13	1.11	1.10	1.14	1.14	1.18			1.14	
	CO_2 (%)		8.0	3.2	3.2	3.2	3.3	2.3	2.6	3.0			2.5	
	O_2 (%)		0.2	1.8	1.0	1.4	0.5	0.6	0.4	0.4			0.4	
	C_nH_{2n} (%)		24.2	31.6	31.4	31.5	29.9	32.1	32.3	28.8			24.2	
	CO (%)		5.2	7.5	7.4	7.5	6.1	2.6	2.5	6.2			3.8	
	C_nH_{2n+2} (%)		50.4	38.5	30.0	34.3	44.0	53.0	51.4	52.8			59.3	
	H_2 (%)		1.39	11.2	16.0	13.6	11.4	9.2	9.7	8.6			9.6	
	N_2 (%)		1.4	5.2	11.0	8.5	5.8	0.2	1.1	0.2			0.3	
	n (%)		2.0	2.0	2.5	2.2	2.6	1.5	1.6	1.0			1.4	

ENCLOSURE (B)5

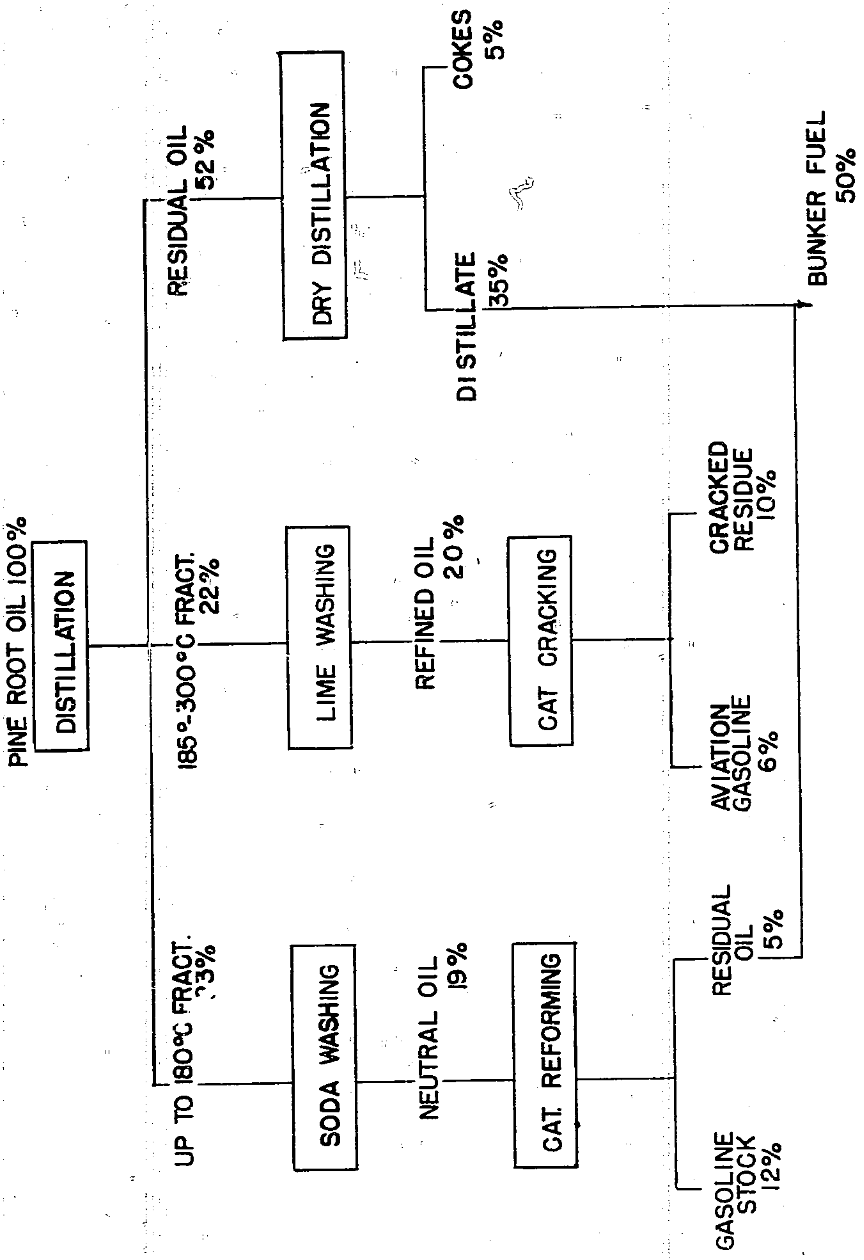


Figure 1(B)5

PLAN FOR COMMERCIAL TREATMENT OF PINE ROOT OIL

ENCLOSURE (B)5

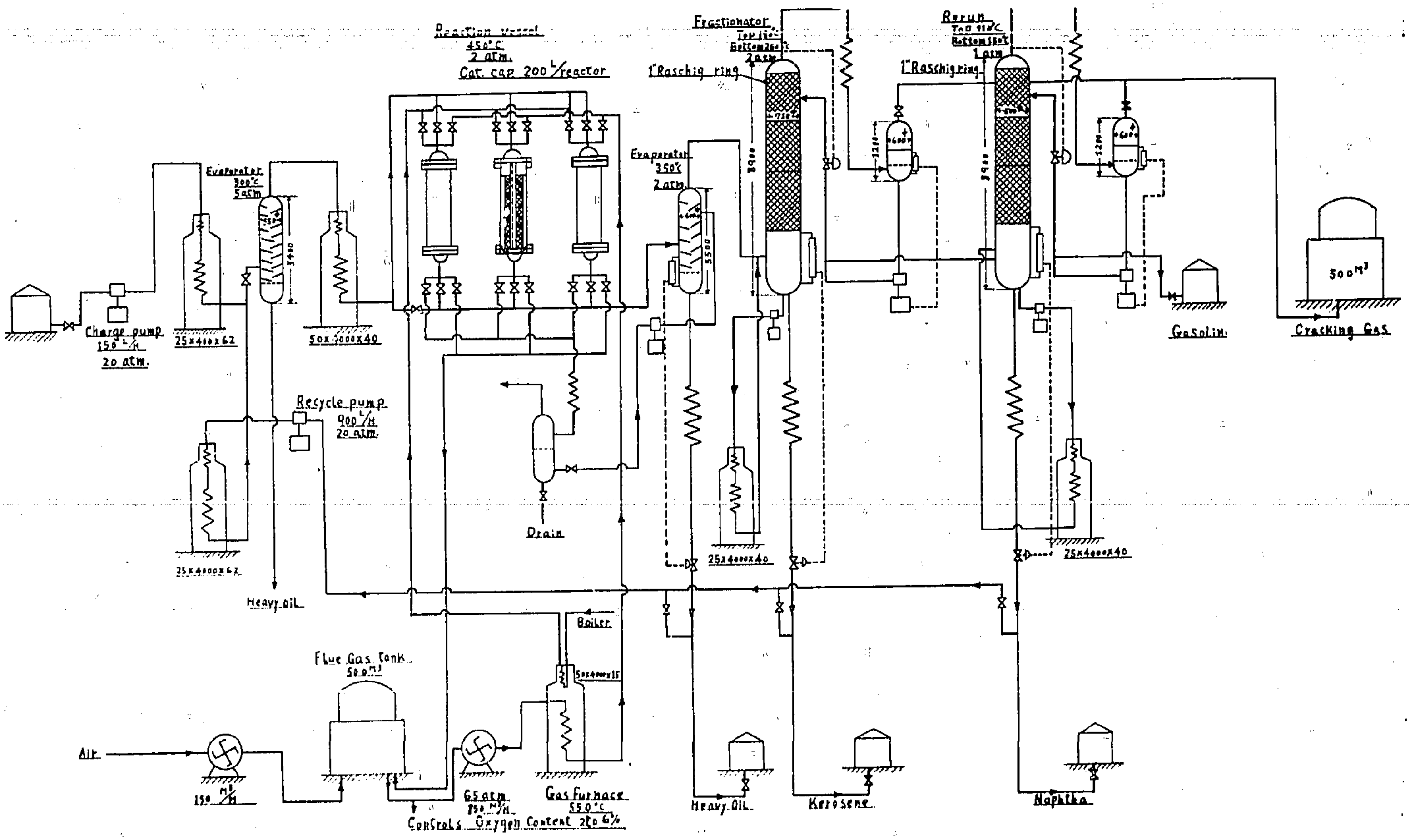


Figure 2(B)5

FLOW CHART OF CATALYTIC CRACKING PILOT PLANT

ENCLOSURE (B)5

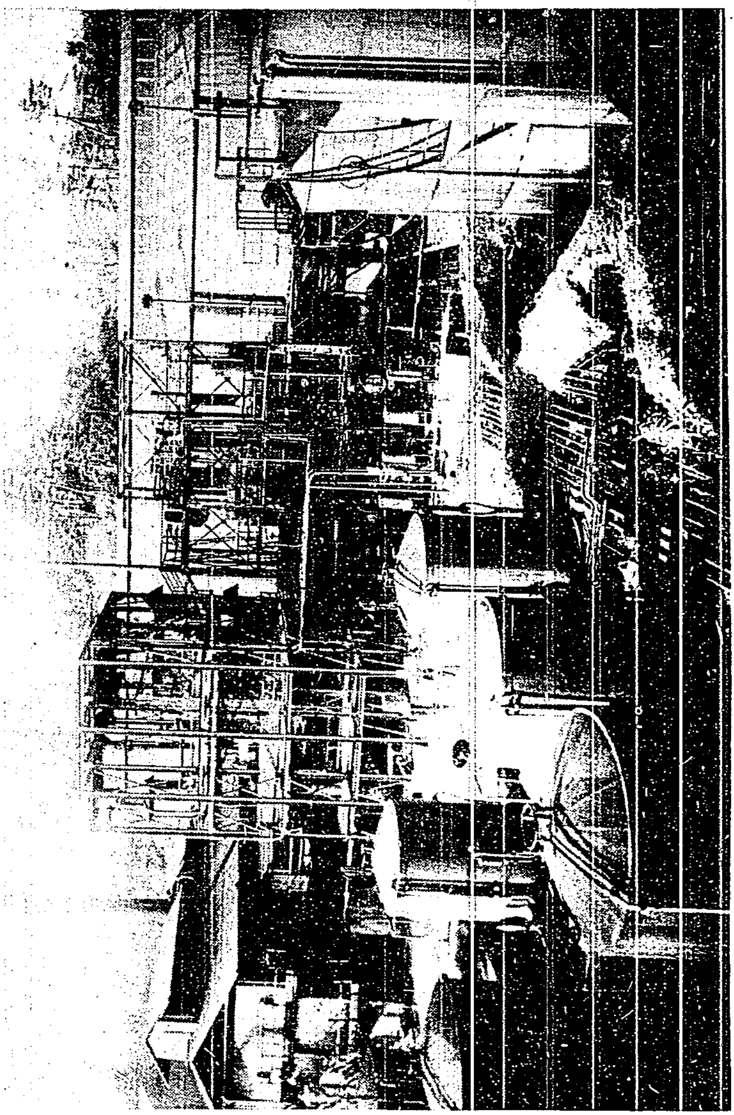


Figure 3(B)5
GENERAL VIEW OF THE CATALYTIC CRACKING PLANT

ENCLOSURE (B)5

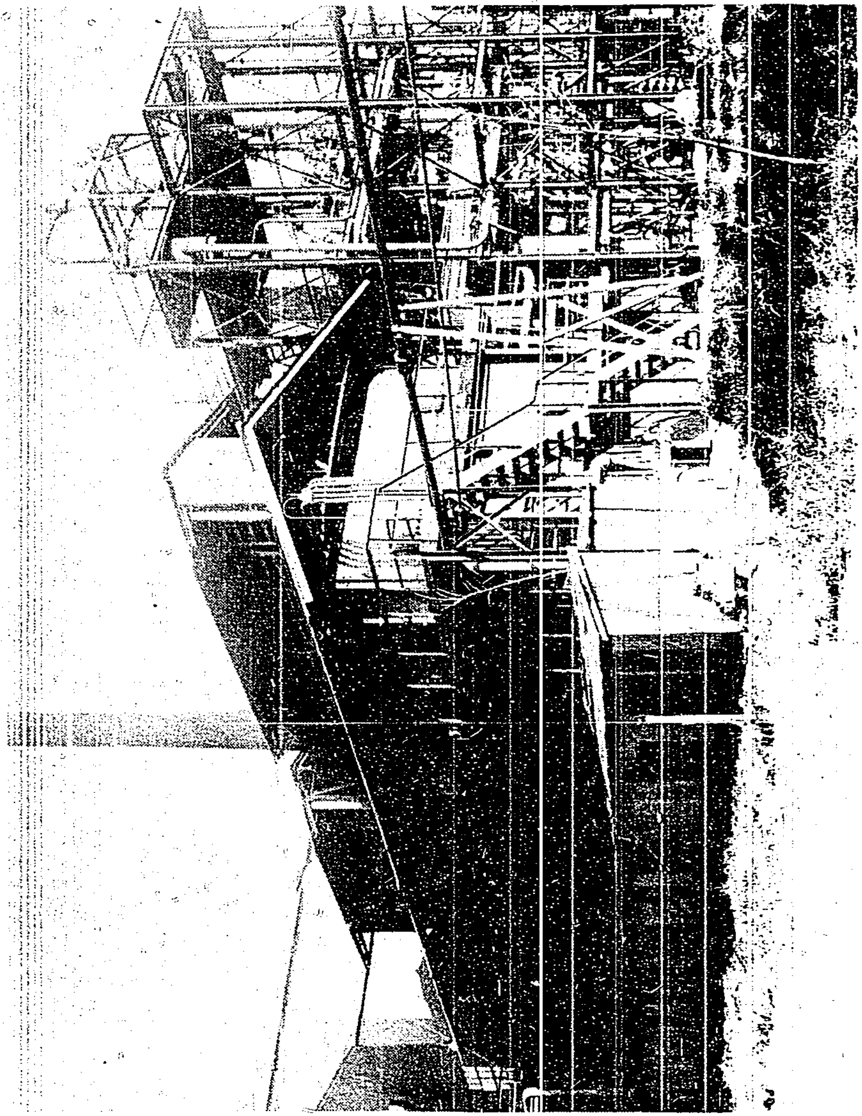


Figure 4(B)5

CLOSE UP VIEW OF THE FURNACE SIDE
OF THE CATALYTIC CRACKING PLANT

ENCLOSURE (B)5

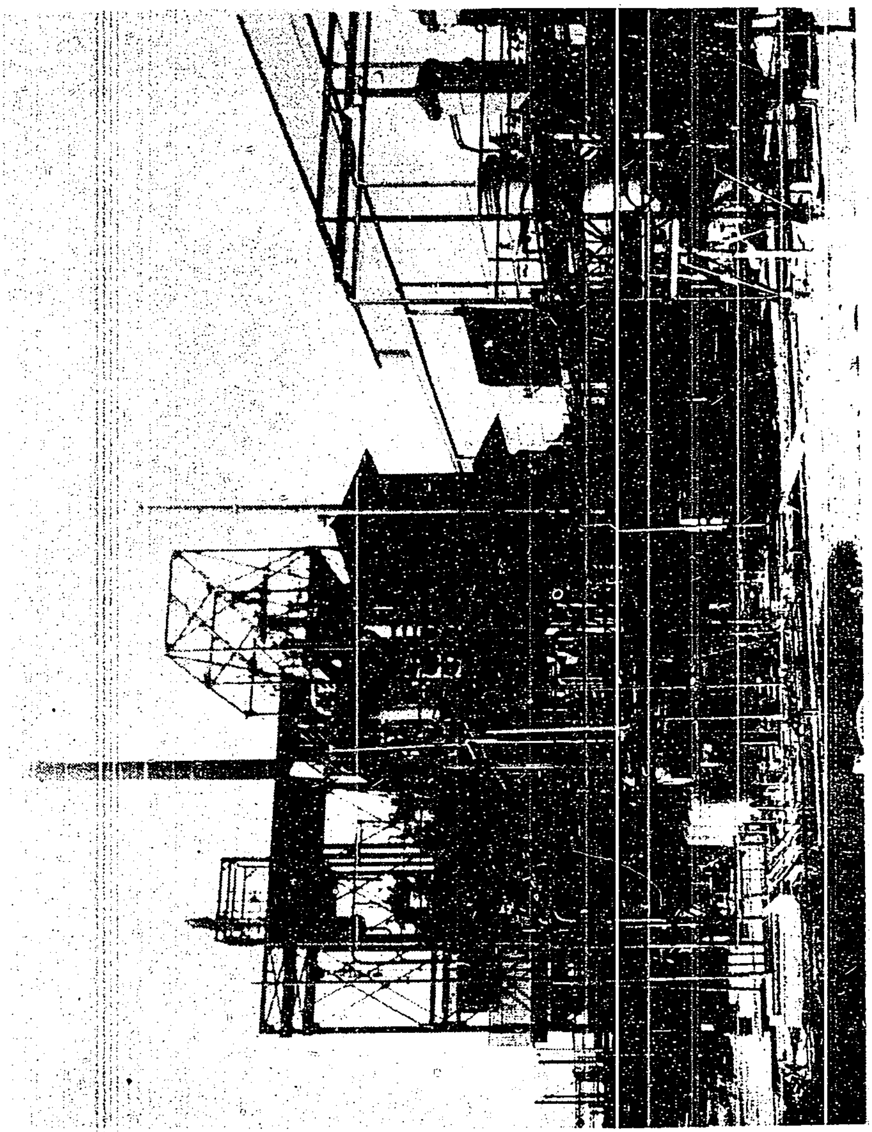


Figure 5(B)5

CLOSE UP VIEW OF THE REACTION CHAMBER
OF THE CATALYTIC CRACKING PLANT

ENCLOSURE (B) 6

DESIGN OF CATALYTIC CRACKING PLANT FOR PINE ROOT OIL

by

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Research Period: 1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)6

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)6

This plant was designed to produce 2,000 lit/day of aviation gasoline by catalytic cracking 10,000 lit/day of the heavy overhead cut from the simplified pine-root oil distillation and coking units.

The design was based on data from the catalytic cracking pilot plant in the research department of this depot. An effort has been made to make the process flow simpler, however, and especially to conserve on the use of special steels, the plant was designed to use carbon steels in the reactors and heating pipes.

Basic design calculations are given in Appendix I and the process flow diagram is given in Plate I(B)6.

APPENDIX I

1. Object of the Plant

This plant is designed to obtain aviation gasoline by the catalytic cracking for which pine oil is used as the crude oil.

2. Plant Capacity

New Charge .... 10,000 lit/day

3. Property of Pine Heavy Oil (Crude)

Specific Gravity	0.896
I.B.P.	122.0°C
10% Point	160.5
20% Point	170.5
30% Point	180.0
40% Point	189.0
50% Point	200.0
60% Point	217.0
70% Point	241.0
80% Point	272.0
90% Point	348.0
E.P.	-

4. Crude Oil Feed Pump

10,000 lit/day = 10,000 x 0.896 = 8,960 kg/day
10,000 lit/day = 417 lit/hr = 6.95 lit/min

This pumping unit shall deliver a normal capacity of 6.95 lit/min at normal and shall be delivered against a discharge pressure of 10 kg/cm^2 with atmospheric suction.

5. Recycle Oil Pump

Basis: Recycle Ratio = 3

6.95 lit/min x 3 = 20.85 lit/min = 1,250 lit/hr

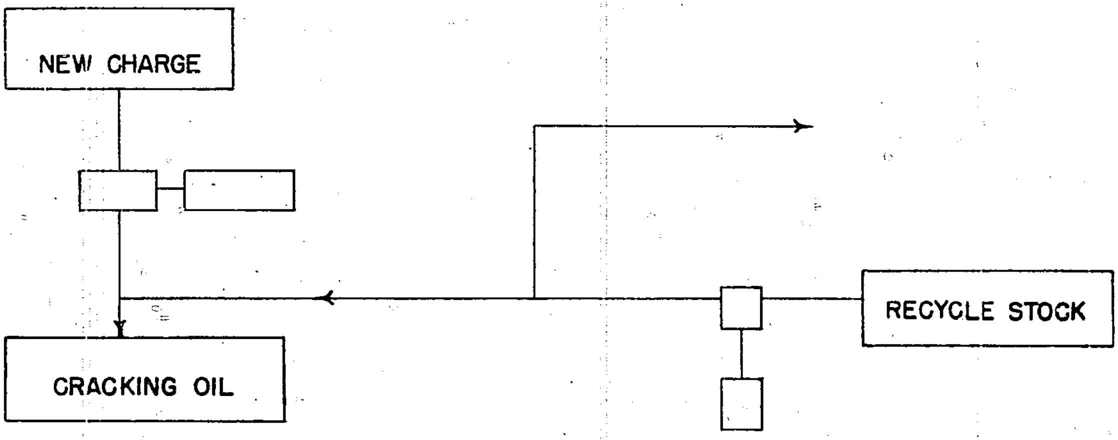
Discharge Pressure	10 kg/cm^2
Suction Temperature	250°C

6. Cracking Oil (Combined Feed)

Recycle stock (10,000 x 3) x 0.832 =	24,950 kg/day
New Charge	8,960 kg/day (+
Total cracking oil	33,910 kg/day

Specific Gravity .... 33,910 ÷ 4000 =	0.848
U.O.P. Characterization Factor	11.4
Mean Molecular Weight	170

ENCLOSURE (B)6



7. Determination of the Temperature of Cracking Combined Feed Oil.

New Charge .... $417 \times 0.896 = 373.6$ kg/hr
Recycle stock .... $1{,}250 \times 0.832 = 1{,}040$ kg/hr
Combined feed .... $373.6 + 1{,}040 = 1{,}414.6$ kg/hr
$= 1{,}667$ lit/hr

Therefore Specific Gravity 0.848

Mean specific heat of recycle stock 0.572

Then
$$0.572 \times 1{,}040 \times (250 - 37) = 126{,}709 \text{ Kcal/hr}$$
$$Cp' \times 1{,}413.6 \times (T_2' - 37) = 126{,}709 \text{ ....(1)}$$

Where
$$Cp' = Cp37 \quad dCp\,(T_2' - 37)$$
$$Cp37 = 0.465 \quad dCp = 0.00097$$

Therefore
$$Cp' = 0.465 + 0.00097\,(T_2' - 37) \text{ .... (2)}$$

Combining equations (1) and (2)
$$(T_2')^2 + 405{,}440T_2' - 108{,}791 = 0$$

Therefore
$$T_2' \doteqdot 184^\circ C$$

8. Temperature of the Flash Chamber.

10% point of combined feed ...... 174°C (345.2°F
70% point of combined feed ...... 252°C (485.6°F
Slope of A.S.T.M. 2.34
Slope of flash, 10 - 70% 1.2
50% boiling point on A.S.T.M. .... 435°F
50% boiling point on flash .... 435°F

100 percent point on linear flash curve
$$435 + 1.2 \times 50 = 495^\circ F \; (257^\circ C)$$

As a check, at 0 percent.
$$435 - 1.2 \times 50 = 375^\circ F \; (190^\circ C)$$

The correction was made at the point where the operating pressure is 5 kg/cm^2 gauge.

100% point $349^{\circ}C\ (660^{\circ}F) \doteqdot 350^{\circ}C$

Since, it must be the temperature of oil of the outlet.

9. Cracking Oil Heater.

If the condition is such that cracking oil does not pass through the exchanger, the heats required to be necessary to heat from 184°C to 350°C at liquid state, are as follows:

$$0.685 \times 1{,}413 \times (350 - 184) = 160{,}740 \text{ Kcal/hr}$$

Where Mean specific heat = 0.685

Assuming the cracking oils which pass through the pipe still are entirely vaporized on the score of the non-vaporized oils remained in the flash chamber are only 3 percent of all by data.

$$75.1 \times (1{,}413 + 2{,}2046) \doteq 234{,}043 \text{ B.T.U./hr} = 59{,}283 \text{ Kcal/hr}$$

Accordingly the total heat is,

$$160{,}740 + 59{,}283 = 220{,}023 \text{ Kcal/hr}$$

Cracking oil (1667 lit/hr)	1413.6 kg/hr
Specific gravity	0.848
Mean M.W.	170
U.O.P. Characterization factor	11.4
Inlet temp.	184°C
Outlet temp.	350°C
Outlet pressure	5 kg/cm^2
Heat required	220,023 Kcal/hr

In this case, the pressure drops of cracking oil throughout the pipe still and another are assumed 5 kg/cm^2 by the data of the pilot plant of the naval laboratory. The furnace capacity is taken as the above purposely, considering the conditions at the start and the allowance but the oils can get the large quantities of heats from the exchanger when operation becomes on stream.

10. Flash Chamber

Temp. of inlet	350°C
Temp. of top of the chamber	300°C
Operating pressure	5 kg/cm^2(gauge)
Feed quantities	1413.6 kg/hr

To calculate the volume of oil vapors in the chamber,

$$1413.6/170 \times 22.4 \times 1/6 \times (273 + 300)/273 = 65.5 \text{ m}^3/\text{h}$$

Assuming the above vapors remain 90 seconds in the chamber.

$$(65.5/60) \times 90/60 = 1.64 \text{ m}^3$$

11. Oil Vapor Heater

Temp. of inlet	300°C
Temp. of outlet	500°C

ENCLOSURE (B)6

Pressure of inlet	5 kg/cm2
Pressure of outlet	2 kg/cm2
Mean specific heat	0.695

$$0.695 \times 1413.6 \times (500 - 300) = 197{,}000 \text{ Kcal/hr}$$

With a 20 percent factor to allow more heating, the heat required is 235,000 Kcal/hr.

12. Reaction Chamber.

Charging quantities = 1,667 lit/hr = 1,413.6 kg/hr
Space velocity = 3

Therefore Catalyzer volume = 1,667 ÷ 3 = 555 lit.

The reduction of catalyzer by means of the reactivation and high temperature is assumed about 15 percent by the data of the pilot plant of the naval laboratory.

$$555 \text{ lit} \times 1.15 = 638 \text{ lit} \doteqdot 640 \text{ lit}$$

Specific gravity of catalyzer 0.75

$$\text{Weight of catalyzer} = 0.75 \times 640 = 480 \text{ kg per tower}$$

Operating pressure	2 kg/cm2
Design pressure	5 kg/cm2
Operating temp.	450 to 500°C
Design temp.	550°C

Materials

Flanges	Cast steel
Shell	Class SB J.E.S.
Bolts and nuts	4-6% Cr. steel

Note: It is really dangerous to use carbon steel plates at the high temperature such as 500°C, but daringly used carbon steel plates on account of the difficulties of getting special steel plates recently such as, Ni-Cr or Cr-Mo. Accordingly, the allowable working stresses must be taken not over 2 kg/mm2, considering the creep stresses.

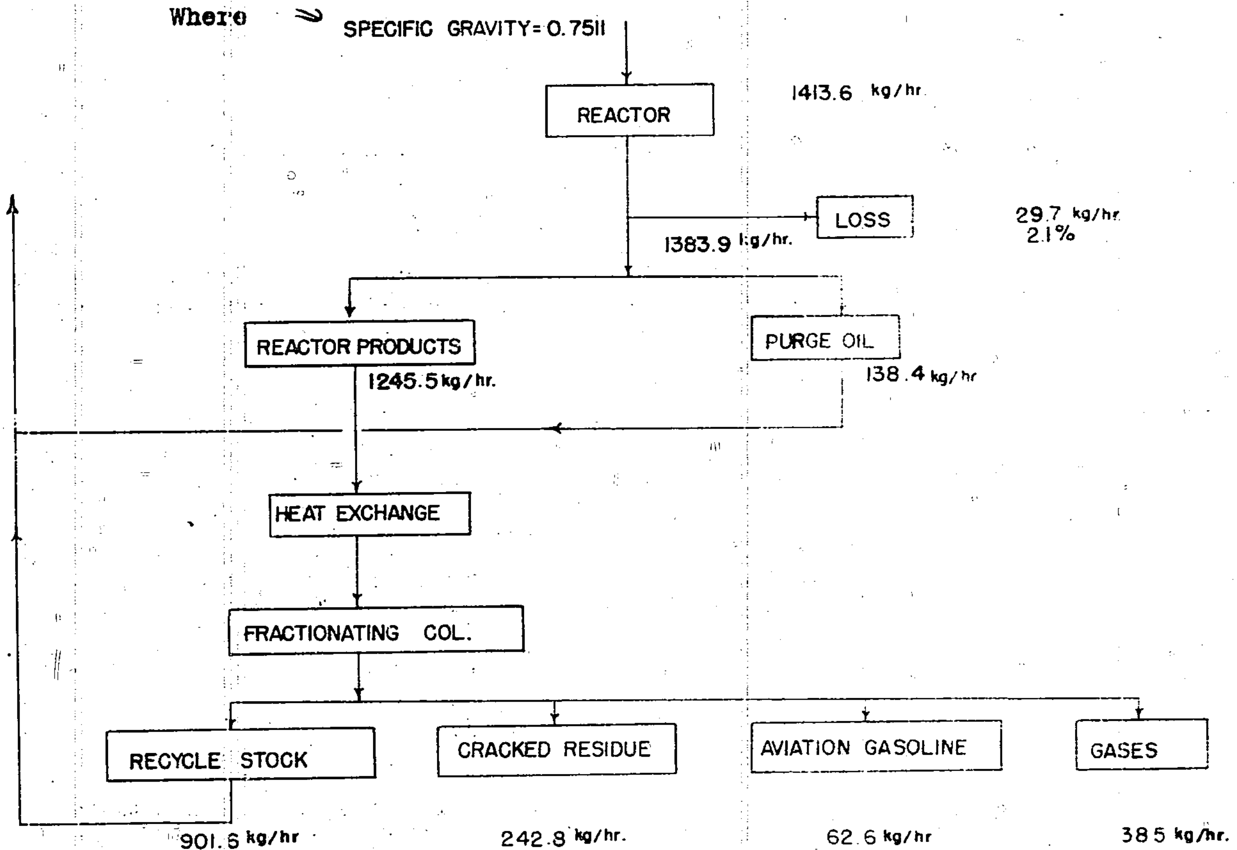
ENCLOSURE (B)6

13. Material Balance in and around the Fractionating Column.

Assuming the aviation gasoline to be 20 percent (vol) of the new charge oil,

417 lit/hr x 0.20 = 83.4 lit/hr = 62.6 kg/hr

Where



Next, assuming the cracked residue is 70 percent (vol) of the new charge oil,

417 lit/hr x 0.70 = 291.9 lit/hr = 242.8 kg/hr

Where

Specific gravity 0.832
Cracked gases and losses .... 38.5 kg/hr

14. Fractionating Column.

Operating pressure .... 1 kg/cm
Operating temp. .... @Top 120°C
Operating temp. .... @Bottom 250°C
Reflux ratio 5
M.W. of oil vapor at the top 120
M.W. of gases at the top 29

Therefore, distillates of Top

Gases .... 38.5 ÷ 29 = 1.33 Kgmol/hr
Vapors .. 62.6 x (5 1) ÷ 120 = 3.13 Kgmol/hr

However $PV = ZnRT$

Where $P = 2$ kg/cm^2 (absolute)

$n_1 = 1.33$ (gases)

$n_2 = 3.13$ (vapor)

$R = 0.094786$

$T = 120 + 273 = 393^\circ K$

$Z_1 = 0.99$ (gas)

$Z_2 = 0.95$ (vapor)

$T_c = 610^\circ F\ (321^\circ C)\quad (321 + 273)^\circ$

Vapor: $TR = 393/594\quad 0.662$

$P_c = 24$ kg/cm^2 (absolute)

$Z_2 = 0.95$

Gas: $T_c = 305^\circ K$

$TR = 393/305 = 1.29$

$P_c = 48$ kg/cm^2 (absolute)

$PR = 2/48 = 0.0417$

$Z_2 = 0.99$

Therefore,

$$\text{Oil Vapor}\quad \frac{0.95 \times 3.13 \times 0.094786 \times 393}{2} = 55.3 \text{ m}^3/\text{hr}$$

$$\text{Gases} = \frac{0.99 \times 1.33 \times 0.094786 \times 393}{2} = 24.4 \text{ m}^3/\text{hr}$$

Total = 79.7

The velocity of the vapors through the column are assumed 0.3 meters per second.

$$D^2 \times 3.1416/4 \times (0.3 \times 3600) = 79.7$$

$$D^2 \times 0.785 \times 1080 = 79.7$$

$$847D^2 = 79.7$$

$$D = 0.31$$

The actual tower diameter that is used for these conditions is taken 450mm as a packed column.

15. Fractionating Column Condenser.

Operating Pressure .... 1 kg/cm^2
Operature temp.
  Inlet .... 120°C
  Outlet .... 37°C (100°F)

Heats to be removed from the gases,

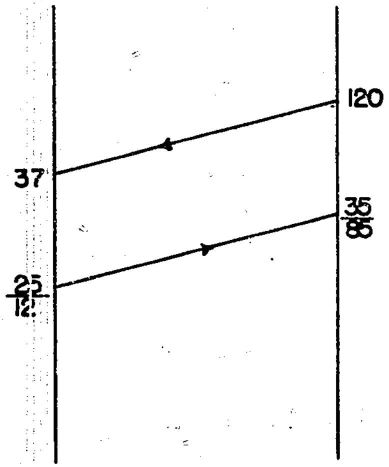
$$0.528 \times 38.5 \times (120 - 37) = 1{,}682.2 \text{ Kcal/hr}$$

Heats to be removed from the vapors,

$$0.553 \times 375.6 \times (120 - 37) = 17{,}239.7 \text{ Kcal/hr}$$

$$131 \text{ B.T.U./lb} \times (62.6 \times 6) \times 2{,}2046 = 108{,}500 \text{ B.T.U./hr}$$
$$= 27{,}400 \text{ Kcal/hr}$$

Total = 46,326.9 Kcal/hr
$\doteqdot$ 46,500 Kcal/hr



$$\Delta T_m = \frac{85 - 12}{2.3 \log 85/12} \doteqdot 37°C$$

$$K = 90 \text{ Kcal/m}^2, °C, \text{ hr}$$

Therefore $A = 46{,}500/(37 \times 90) \doteqdot 14 \text{ m}^2$

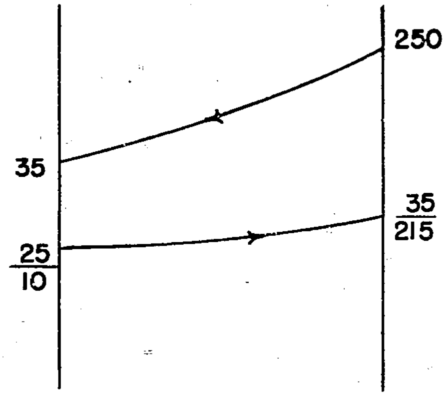
Total surface 20 m^2; Box condenser type.

Cooling water: $W = 46{,}500/(35-25) = 4{,}650$ kg/hr

16. Fractionating Column Bottom Cooler.

Cracked residues .. 291.9 lit/hr = 242.8 kg/hr
Specific gravity 0.832
Operating pressure .... 1 kg/cm^2
Operating temp.
  Inlet .... 250°C
  Outlet .... 37°C

$$0.572 \times 242.8 \times (250 - 37) = 29{,}581 \text{ Kcal/hr} \doteqdot 30{,}000$$



$$dTm = \frac{215 - 10}{2.3 \log 215/10} = 67^{\circ}C$$

K = 60 Kcal/m^2, hr, °C

Therefore $A = 30{,}000/(67 \times 60) \doteqdot 7.5 \ m^2$

The actual cooling surface is taken 10 m^2.

Cooling water: W = 30,000/(35 - 25) = 3,000 kg/hr @normal

17. Reflux Oil Accumulator.

Vapor condensed, $375.6 \div 0.7511 = 500$ lit/hr

Gases, $\frac{0.99 \times 1.327 \times 0.094786 \times 310}{2} = 19.3 \ m^3/hr$

Assuming the accumlator keeps reflux oil during 10 minutes in ½ volume of it.

$$500/60 \times 10 \times 2 = 167 \text{ lit}$$

Then the volume of the accumulator is necessary to occupy 167 lit or over.

18. Reflux Oil Pump.

This pumping unit shall deliver a normal capacity of 8.34 lit/min that volume at 37°C and shall be delivered against a discharge pressure of 5 kg/cm^2 suction.

19. Heat Exchanger.

Heat Balance

a. Heat contents of the vapors leaving the reactor system.

Basis: 100°F

Liquid: 0.61 x 1,245.5 x (300 - 100) = 152,000 Kcal/hr

Vapor: 0.695 x 1,245.5 x (500 - 300) = 173,000 Kcal/hr

ENCLOSURE (B)6

Latent heat:

$$75 \times 1{,}245.5 \times 2{,}2046 = 205{,}500 \text{ B.T.U./hr} = 51{,}800 \text{ Kcal/hr} \;(+$$

Total =376,800 Kcal/hr

b. <u>Heats to be removed</u>.

Top vapors and gases	46,500 Kcal/hr
Bottom cracked residues	30,000 Kcal/hr
Bottom recycle oils	111,000 Kcal/hr
Heat losses	56,500 Kcal/hr
Total	244,400 Kcal/hr

Heat loss is assumed about 15 percent of the total heat.

$$376{,}800 \times 0.15 = 56{,}500 \text{ Kcal/hr}$$

Heat to be exchanged

$$376{,}800 - 244{,}400 = 132{,}400 \text{ Kcal/hr}$$

a. Cold Fluid: (New charge and recycle oil)

1,413.6 kg/hr = 1,667 lit/hr

Specific gravity	0.848	35.5 A.P.I.
M.W.		170
Inlet temp.		180°C

If the outlet temperature is assumed nearly 300°C and not to be vaporized,

$$0.68 \times 1{,}413.6 \times (t_1 - 180) = 132{,}400$$

then $t_1 = 318°C$

In this case, taken 300°C

b. Hot Fluid: (Cracked oil and vapor)

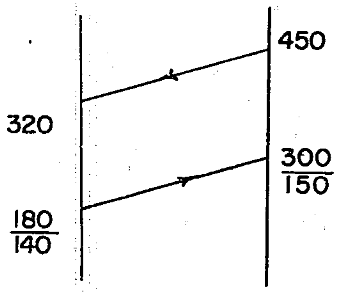
If the outlet temperature assumed nearly 300°C and not to be condensed.

$$0.695 \times 1{,}245 \times (500 - t_2) = 132{,}000$$

then $t_2 = 345°C$

In this case, taken 320°C.

So that, the temperature of feed oil to the fractionating column is about 320°C, but the temperature drops throughout the piping and other heat losses are obscure. However, it is assumed as follows, and taken a larger heating surface and should be regulated the feed temperature by adjusting the bypath valves.



dTm $= 145^{\circ}C$

K $= 120$ Kcal/m^2, hr, $^{\circ}C$

Therefore A $= 132{,}400 : (145 \times 120)$

$= 7.6$ m^2

With a safety factor, the surface is 15 m^2.

20. Reactivations of Catalyzer.

a. Carbon deposits are assumed 8 percent (wt) to the new charge oil depend upon the data of the naval laboratory.

$$6960/24 \times 0.08 = 29.9 \text{ kg/hr} \doteqdot 2.49 \text{ kgmol/hr}$$

Oxygen is necessary 1 mol per mol of carbon theoretically, therefore necessary air amounts are as follows:

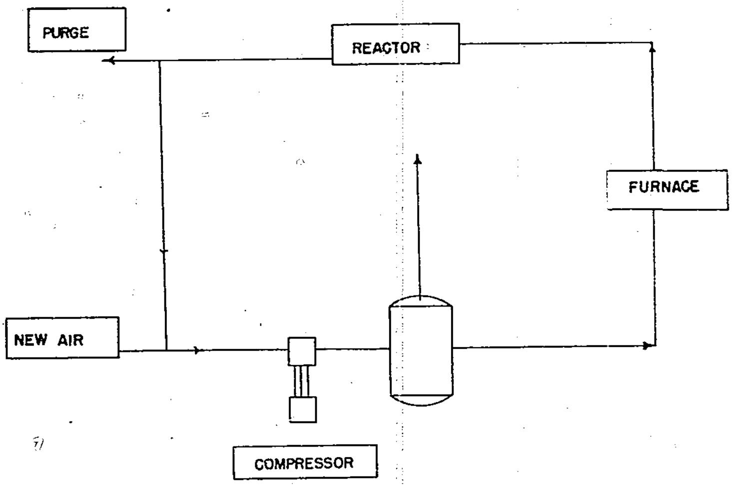
$$2.49/0.21 \times 22.4 = 265 \text{ m}^3\text{/hr}$$

With a 33 percent to allow the efficiency of combustion the necessary air amounts are 800 m^3 per hour.

b. The minimum air quantities to be necessary to keep uniformly the distribution of the temperature in the reactors is required about 600 600 m^3 per 1,000 kg of cracking stocks,

then $600 \times 33.910/24 \doteqdot 850$ m^3/hr

Having in mind (1) and (2), the capacity of the air compressor is determined 15 m per minute.



ENCLOSURE (B)6

Note: The reactors should be used three interchangeably.

21. Reactivating Gas Heater.

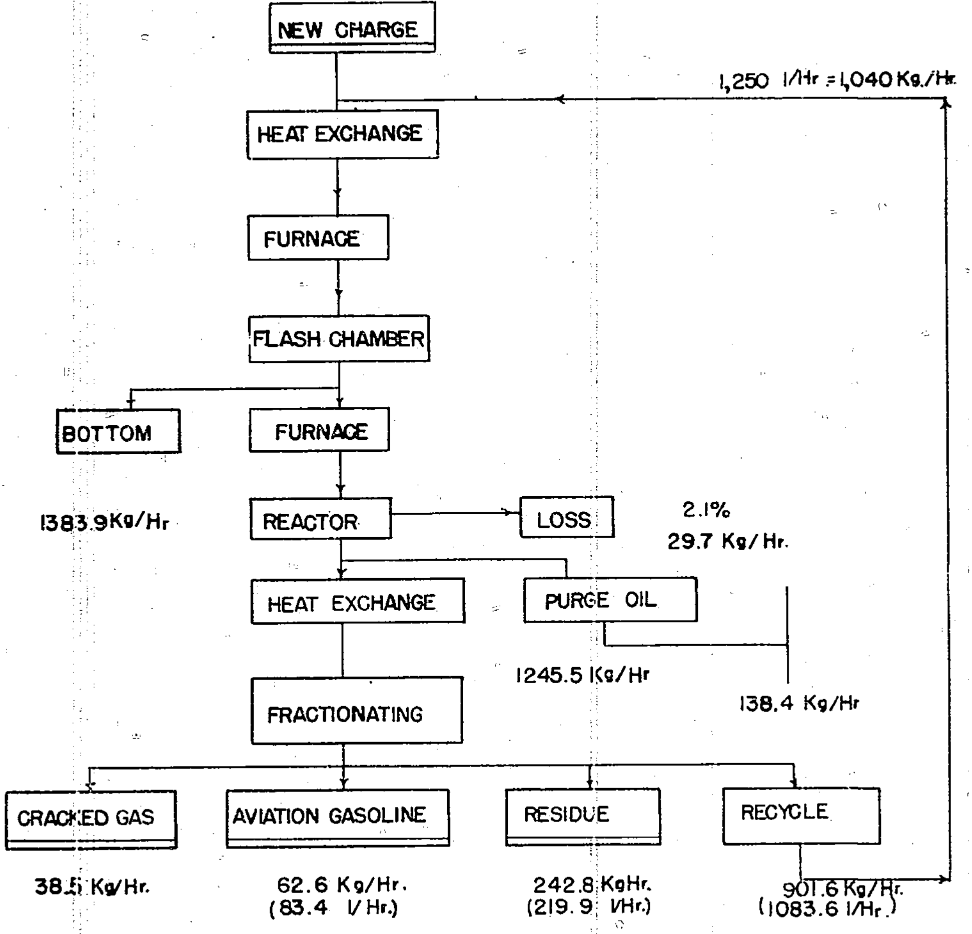
Quantities	850 m^3/hr
Operating pressure	5 kg/cm^2 to 2 kg/cm^2
Inlet temp.	25 °C
Outlet temp.	500°C

Heat required:

$$0.33 \times 850\ (500 - 25) = 133{,}000\ \text{Kcal/hr} \fallingdotseq 150{,}000\ \text{Kcal/hr}$$

Normal Operating Capacity 10,000 lit/day

417 l/Hr = 373.6 l/Hr



=10% =16.8%

Products	% to new charge
Aviation gas	20
Cracked gas	10
Residue	70

RESTRICTED

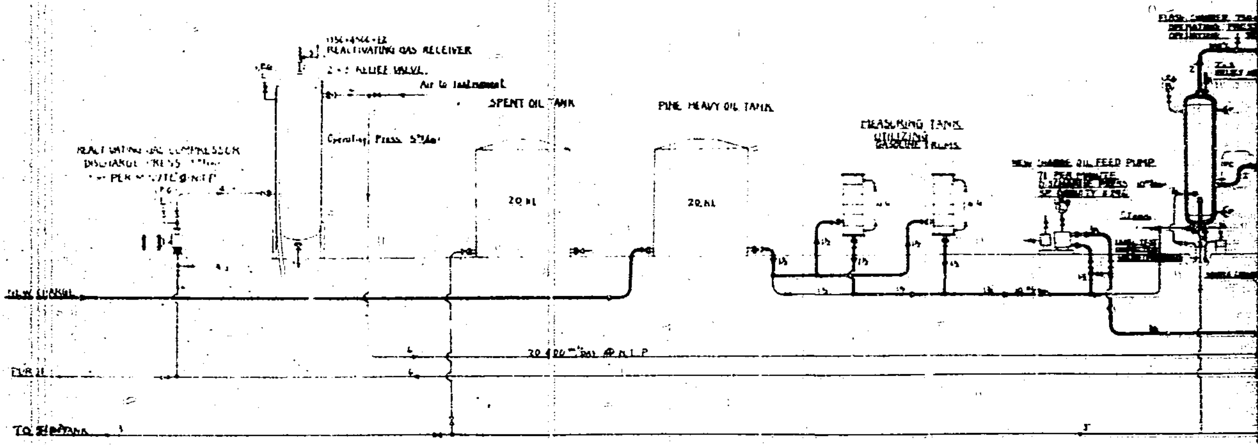

REACTIVATING GAS RECEIVER
2 RELIEF VALVE
Air to instrument
Operating Press. 5 kg/cm²
SPENT OIL TANK
20 KL
PURE HEAVY OIL TANK
20 KL
MEASURING TANKS UTILIZING GASOLINE DRUMS
REACTIVATING GAS COMPRESSOR
DISCHARGE PRESS.
PER MINUTE @ N.T.P.
NEW CHARGE OIL FEED PUMP
PER MINUTE
DISCHARGE PRESS.
SP. GRAVITY
FLASH CHAMBER
OPERATING PRESS.
NEW CHARGE
FUR. II
TO SLOP TANK
20,400 m³/Day @ N.T.P.

PLATE I (B) 6

FLOW DIAGRAM OF CATALYTIC CRACKING PLANT

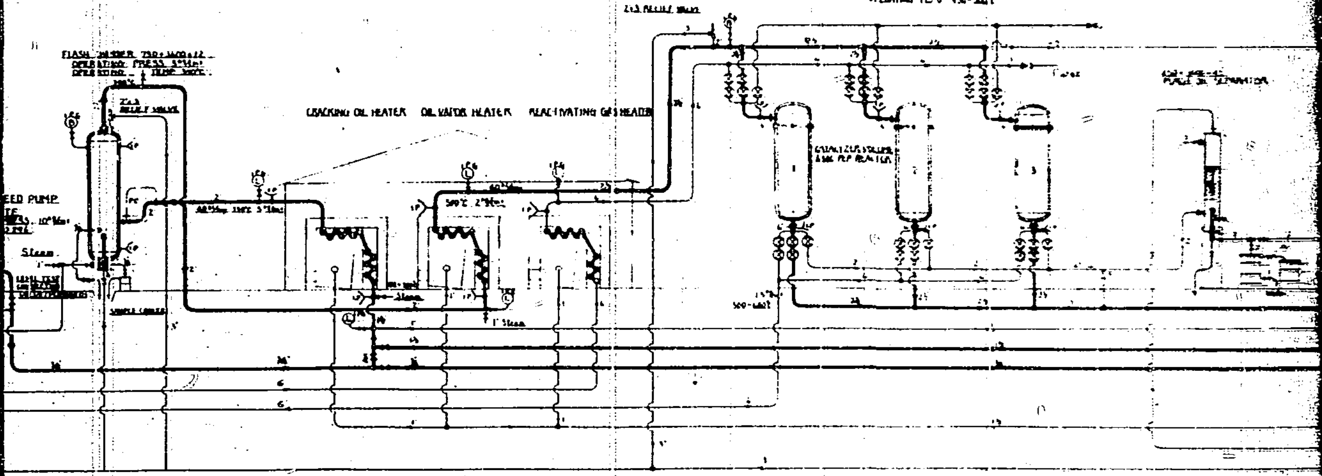
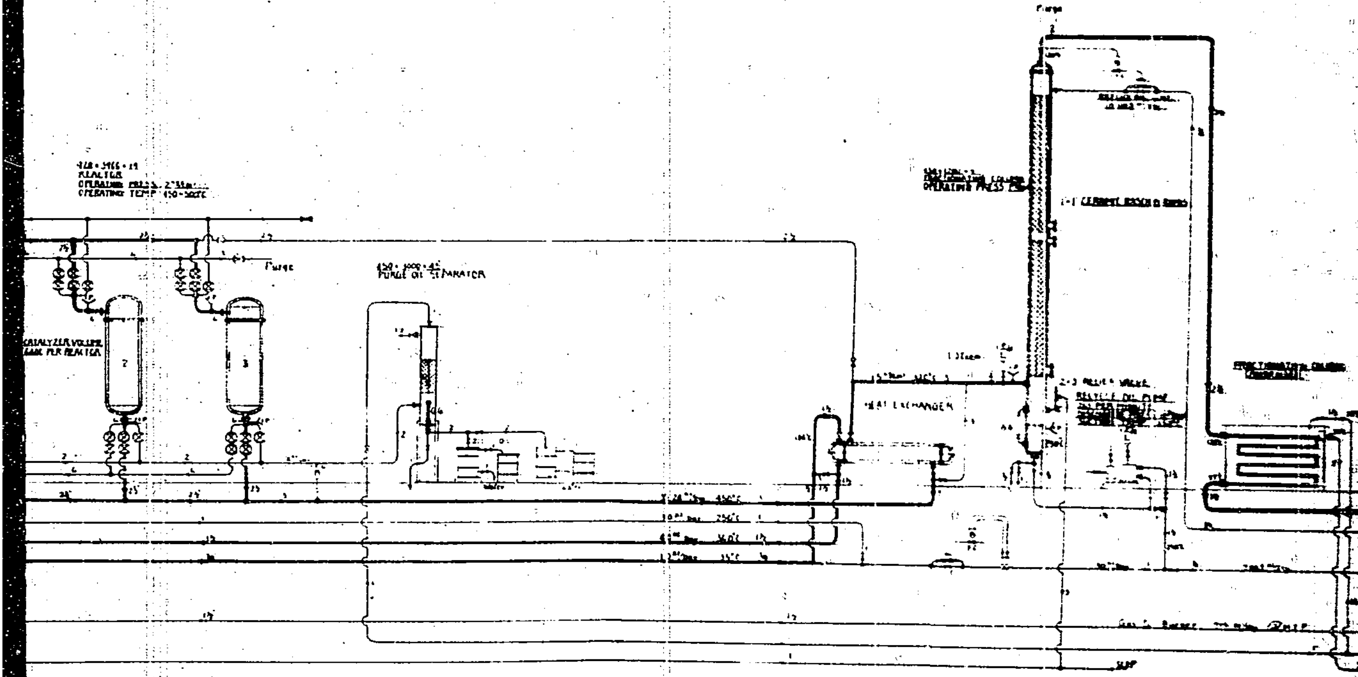
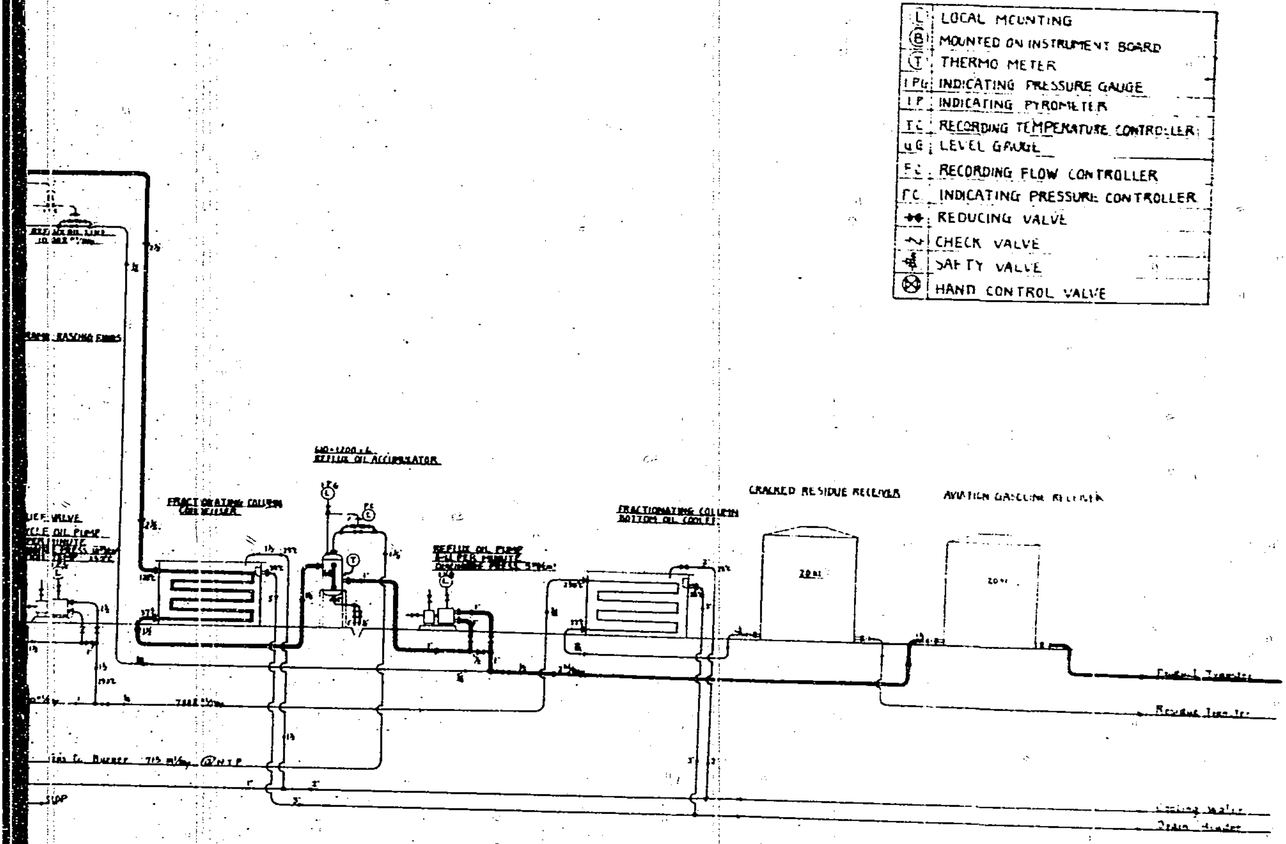


PLATE I (B) 6

FLOW DIAGRAM OF
CATALYTIC CRACKING PLANT





L	LOCAL MOUNTING
B	MOUNTED ON INSTRUMENT BOARD
T	THERMO METER
IPG	INDICATING PRESSURE GAUGE
IP	INDICATING PYROMETER
TC	RECORDING TEMPERATURE CONTROLLER
LG	LEVEL GAUGE
FC	RECORDING FLOW CONTROLLER
PC	INDICATING PRESSURE CONTROLLER
⧓	REDUCING VALVE
~	CHECK VALVE
⚲	SAFTY VALVE
⊗	HAND CONTROL VALVE

ENCLOSURE (B) 7

STUDIES ON THE MANUFACTURE OF AVIATION GASOLINE BY HIGH PRESSURE HYDROCRACKING OF PINE ROOT OIL

by

CHEM. ENG. LIEUT.
S. INABA

Research Period:
Dec. 1944 to Aug. 1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)7

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)7

SUMMARY

This project was established to determine the optimum operating conditions for production of aviation gasoline by high pressure hydrocracking of pine root oil. Pilot plant tests were essentially completed and the process was ready for large scale development to increase the supply of high octane aviation gasoline. These experiments were made on a pine root oil cut of 185-300°C in a small continuous pilot plant, using $MoO_3 + NiO$ catalyst, under reaction conditions of 0.15-1.0 space velocity, hydrogen pressure of 200 kg/cm^2 and temperature of 400-450°C. An aviation gasoline, with a 95 octane number (with 0.15% of Tetra Ethyl Lead), was obtained in yield of about 50% when SV was 0.5, and 28-30% when SV was 1.0.

I. INTRODUCTION

A. History of Project

The investigation of pine root oil as a source of aviation gasoline started at the end of 1944 as a result of the urgent demands of the war. Since satisfactory aviation fuel could not be obtained directly from the product of dry distillation of pine roots, refining methods of high pressure hydrocracking and catalytic cracking were investigated. For the hydrocracking studies described in this report, the oil fraction boiling from 185-300°C, obtained by dry distillation of pine roots, was used as raw material. (The fraction, boiling below 185°C was treated by simple catalytic reforming.) Since very few large scale hydrocracking plants were installed in Japan, these experiments were carried forward with great speed. Pine root oil has many special characteristics, for example, high content of acidic matter and resins, and it was most important to determine the operating conditions for a smooth working process, especially to find a strong and active catalyst with long life. It was expected that a high octane aviation gasoline composed of naphthenic or paraffinic hydrocarbons, would be obtained by the hydrocracking of pine root oil.

B. Research Personnel Working on Project

Chem. Eng. Lt. Comdr. R. YUMEN
Chem. Eng. Lt. Comdr. T. IIJIMA
Chem. Eng. Lieut. K. SONE
Chem. Eng. Lieut. S. INABA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

Studies were first made in small rotating autoclave to determine the proper conditions for hydrocracking of pine root oil, and finally continuous tests were made in a small scale pilot plant with a 3-10 liters reaction chamber. This plant is described by Chem. Eng. Lieut. K. SONE in his "Study on Hydrocracking of High Temperature Coal Tar".

B. Properties of Raw Material

Pine root oil boiling at 185-300°C, with a brownish-black color, was used as raw material. Properties of this stock are given below:

ENCLOSURE (B)7

Specific Gravity (d_4^{15})	0.9495
I.B.P. (°C)	165
10%	184
20%	192
30%	203
40%	215
50%	234
60%	262
70%	288
80%	299
90%	331
Final	332
Acidic Substance (% determined with 10% NaOH solution)	24.4

C. <u>Reaction Conditions</u>

First, it was established by many tests in small autoclaves (five liters capacity), that the best conditions for the reaction were a temperature of 420-450°C and a hydrogen pressure of 200 kg/cm^2, using either Nickel and Molybdenum Oxide (NiO + MoO$_3$) or Molybdenum Sulphide (MoS$_3$) catalyst, refer to Tables I(B)7 and II(B)7. Although the latter catalyst was better from the standpoint of octane number, the former had a longer period of activity, since the sulphur in MoS$_3$ catalyst escaped within a few days, resulting in loss of activity. Under the condition of 100 kg/cm^2 of hydrogen pressure, the products were not satisfactory for aviation gasoline, having a comparatively high content of acidic substances (Table I(B)7). By increasing the pressure to 200 kg/cm^2, the properties of products changed rapidly and very superior aviation gasoline was obtained, with 95 octane number and almost no content of acidic substance. The yield of aviation gasoline was about 70% of total cracked product, and 50% of the raw material in the autoclave tests. In pilot plant tests, the yield was about 50% of the product, and about 40% of the raw material for a space velocity of 0.5. When SV was increased to 1.0, the yield dropped to 33% of the product, and 28% of the raw material. (Refer to Tables I(B)7, II(B)7, and III(B)7.)

The procedure for the pilot plant test was as follows. First, the hydrogen pressure was increased gradually by the compresser, until the pressure of the apparatus,--Reaction Chamber, Preheater, High Pressure Separater, Pipes, etc.--reached 200 kg/cm^2. The reaction chamber temperature was brought to 300°C by electric heating, and oil was gradually charged. After about six hours, 400°C temperature used in the first run was reached. The temperature was raised as slowly as possible to 470°C, which was the maximum temperature for this type apparatus, in order to maintain catalyst activity for one-two months at least. The experimental results (Table III(B)7) were regarded as a satisfactory basis for large scale plant operations at the Second or Third Naval Fuel Depot.

D. Yield and material balance for pilot plant test are given in Figure 1(B)7 and Figure 2(B)7.

E. It is understood that a large scale plant performance test in July 1945 at the Third Naval Fuel Depot showed almost the same results as obtained in these pilot plant experiments. It was said that in this plant test aviation gasoline with 91 octane number was obtained in yield of about 50% of pine root oil charged. This test only lasted for one-two weeks. Longer periods of operation were planned, however, to assist in meeting the great demand for aviation fuel in Japan.

ENCLOSURE (B)7

III. CONCLUSIONS

High pressure hydrocracking is one of the best methods for obtaining high octane aviation gasoline from pine root oil. However, since very few large hydrocracking plants were installed in Japan, simpler catalytic reforming methods were also to be adopted, though producing less satisfactory products. None of these methods actually resulted in large scale production of aviation gasoline from pine root oil, however. It has been definitely shown that an aviation gasoline of 91-95 octane number (with 0.15% of lead) can be produced in yield of about 50% from pine root oil by means of high pressure hydrocracking. Optimum reaction conditions are hydrogen pressure 200 kg/cm^2, temperature 400 to 450°C, space velocity 0.5-1.0 and using Nickel and Molybdenum ($NiO + MoO_3$) catalyst. In the case of Molybdenum Sulphide (MoS_3), further investigation is necessary with regard to prolonging catalyst life.

Table I(B)7
RESULTS OF AUTOCLAVE TESTS AT 100 kg/cm^2

			Experiment No.	
			1	2
Catalyst			$NiO_4 + MoO_3$	MoS_3
Reaction Conditions	Hydrogen Pressure (kg/cm^2)		100	100
	Temperature (°C)		350	350
	Time (hr)		3	5
Products	Absorbed Hydrogen (wt % of Raw Oil)		2.3	2.3
	Yield of Cracked Oil (wt% of Raw Oil)		81.9	83.4
	Yield of Water (wt % of Raw Oil)		6.0	7.1
	Acidic Matter (vol % in Cracked Oil)		7.0	6.0
	Specific Gravity of Cracked Oil (d_4^{15})		0.846	0.832
	I.B.P. of Cracked Oil (°C)		88	46
	10%		153	94
	50%		177	154
	90%		270	224
	97%		280	274
	Final		283	315
	Yield to	150°C Fraction (vol %)	3	42
		160°C Fraction (vol %)	21	53
		170°C Fraction (vol %)	36	65
		200°C Fraction (vol %)	72	86
Aviation Gasoline Cut	Yield from Cracked Oil (vol %)		7.0	42.0
Octane No. of Aviation Gasoline	Clear		76.0	75.0
	With 0.15% of Lead		93.6	94.0

ENCLOSURE (B)7

Table II(B)7
RESULTS OF AUTOCLAVE TESTS AT 200 kg/cm^2

		Experiment No.	
		1	2
Catalyst		$NiO + MoO_3$	MoS_3
Reaction Conditions	Hydrogen Pressure (kg/cm^2)	200	200
	Temperature (°C)	450	450
	Time (hr)	3	3
Products	Absorbed Hydrogen (wt % of Raw Oil)	4.14	4.1
	Yield of Cracked Oil (wt % of Raw Oil)	76	74
	Water (wt % of Raw Oil)	6.8	8.34
	Acidic Matter (vol % in Cracked Oil)	0.4	0.6
	Specific Gravity of Cracked Oil (d_4^{15})	0.812	0.7646
	I.B.P. of Cracked Oil (°C)	48	20
	10%	86	63.5
	50%	130	120
	90%	220	185
	97%	264	210
	Final	293	230
	Yield to 150°C Fraction (vol %)	64	73
	160°C Fraction (vol %)	75	85
	170°C Fraction (vol %)	69	79
	200°C Fraction (vol %)	86	94
Aviation Gasoline Cut	Yield from Cracked Oil (vol %)	70	87
	Acidic Matter in Aviation Gasoline (vol %)	0	0
	Specific Gravity (d_4^{15})	0.804	0.7616
	I.B.P. (°C)	62	23.4
	10%	94	62.5
	50%	117	104.5
	90%	147	147.5
	97%	160	165.5
	Final	170.4	168.0
Composition of Aviation Gasoline	Unsaturate Hydrocarbon (vol %)	3.0	0
	Aromatic (vol %)	31.3	24.0
	Naphthenic	51.4	30.4
	Paraffinic	24.3	35.6
	Aniline Point (°C)	49.5	58.0
Octane No. of Aviation Gasoline	Clear	80.6	78.0
	With 0.15% of Lead	95.7	96.7

Table III(B)7
RESULTS OF PILOT PLANT TESTS*

		Experiment No.				
		1	2	3	4	5
Catalyst		NiO + MoO$_3$	NiO + MoO$_3$	NiO + MoO$_3$	NiO + MoO$_3$	NiO + MoO$_3$
Reaction Conditions	Hydrogen Pressure (kg/cm^2)	200	200	200	200	200
	Temperature (°C)	420	430	430	450	460
	Space Velocity (Liquid Oil)	0.7	0.5	0.5	0.7	1.0
	Charged Oil (lit/hr)	2.0	1.5	1.5	2.0	3.0
	Charged Hydrogen Gas (m^3/hr)	2.0	1.8	1.8	1.6	2.8
	Run Length (hr)	6	6	6	6	6
Products	Absorbed Hydrogen (wt % of Charged Oil)	6.0	4.3	5.0	3.9	4.8
	Yield of Cracked Oil (vol % of Charged Oil)	89.5	85.3	95.4	103.0	92.0
	Yield of Cracked Oil (wt % of Charged Oil)	73.8	71.0	78.3	86.7	80.0
	Water in Charged Oil (wt %)	3.1	5.0	3.0	2.9	4.1
	Acidic Matter in Cracked Oil (vol %)	0.4	0	0	0	0.3
	Specific Gravity of Cracked Oil (d^{15}_{4})	0.785	0.782	0.778	0.80	0.839
	I.B.P of Cracked Oil (°C)	23.0	30.5	29	31	26
	10%	75.5	77	78	91.5	100
	50%	147	142	156	157	164
	90%	236	195	203	241	273
	97%		286	287	318	
	Final	297	286	295	318	339
Residue Gas Composition	CO$_2$ (vol %)	0	0.2	0.3	0.1	0.2
	O$_2$	0.2	0.3	0.5	0.2	0.6
	C$_n$H$_{2n}$	0.9	0.9	0.6	1.2	0.6
	CO	0.1	0.4	0.4	0.3	0.2
	C$_n$H$_{2n+2}$	7.9	16.5	9.82	6.7	17.7
	H$_2$	85.0	78.2	86.42	90.2	74.9
	N$_2$	5.9	3.5	1.96	1.3	5.8
	n (Carbon Number)		0.9		1.2	
Aviation Gasoline Cut	Specific Gravity (d^{15}_{4})	0.7727	0.7567	0.7463	0.7717	0.7488
	Yield from Cracked Oil (wt %)	45.3	51.4	44.6	40.0	35.0
	I.B.P. (°C)	32.0	30.2	26.0	34.0	36.0
	10%	65.0	60.0	59.0	70.5	75.0
	50%	112.5	107	117	110	115
	90%	159	158	160	157	160
	97%	170	169	173	170	173.5
	Final	180	185	209	207	192
	Acidic Matter in Aviation Gasoline (vol %)	0	0	0	0	0
Composition of Aviation Gasoline	Unsaturate Hydrocarbon (vol %)	0.9	1.5	3.0	1.0	1.2
	Aromatic	15.6	13.8	20.0	11.9	12.3
	Naphthenic	40.6	59.0	40.5	56.9	54.2
	Paraffinic	42.9	25.7	36.5	30.2	32.3
	Aniline Point (°C)	49.1	55.6	54.2	50.2	50.0
Octane No. of Aviation Gasoline	Clear	75.2	76.0	72.5	78.1	78.5
	With 0.15% of Lead	96.2	97.6	92.0	96.6	95.4

*Recycle oil used as raw material

ENCLOSURE (B)7

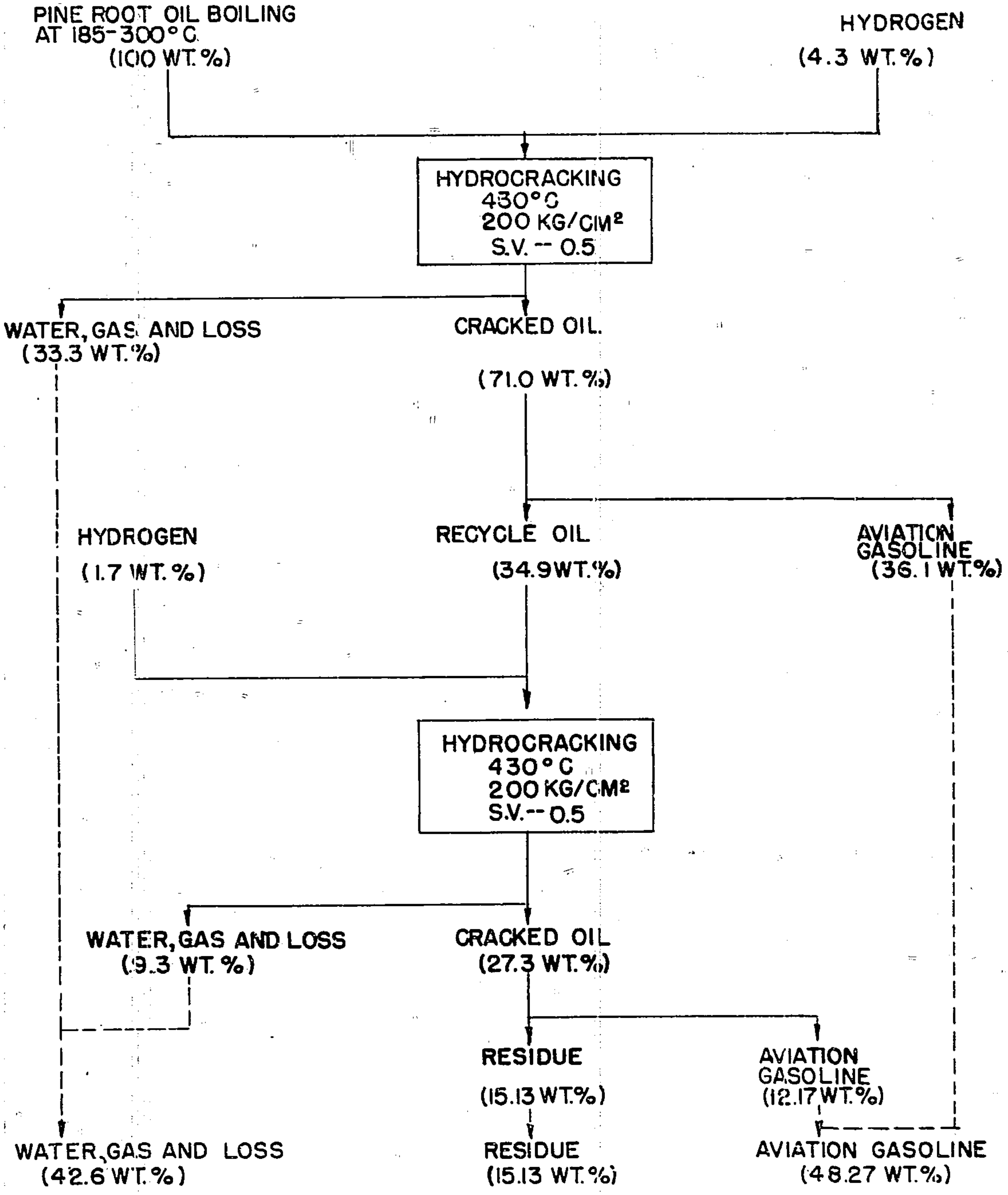


Figure 1(B)7

YIELD AND MATERIAL BALANCE

(S.V. of 0.5)

ENCLOSURE (B)7

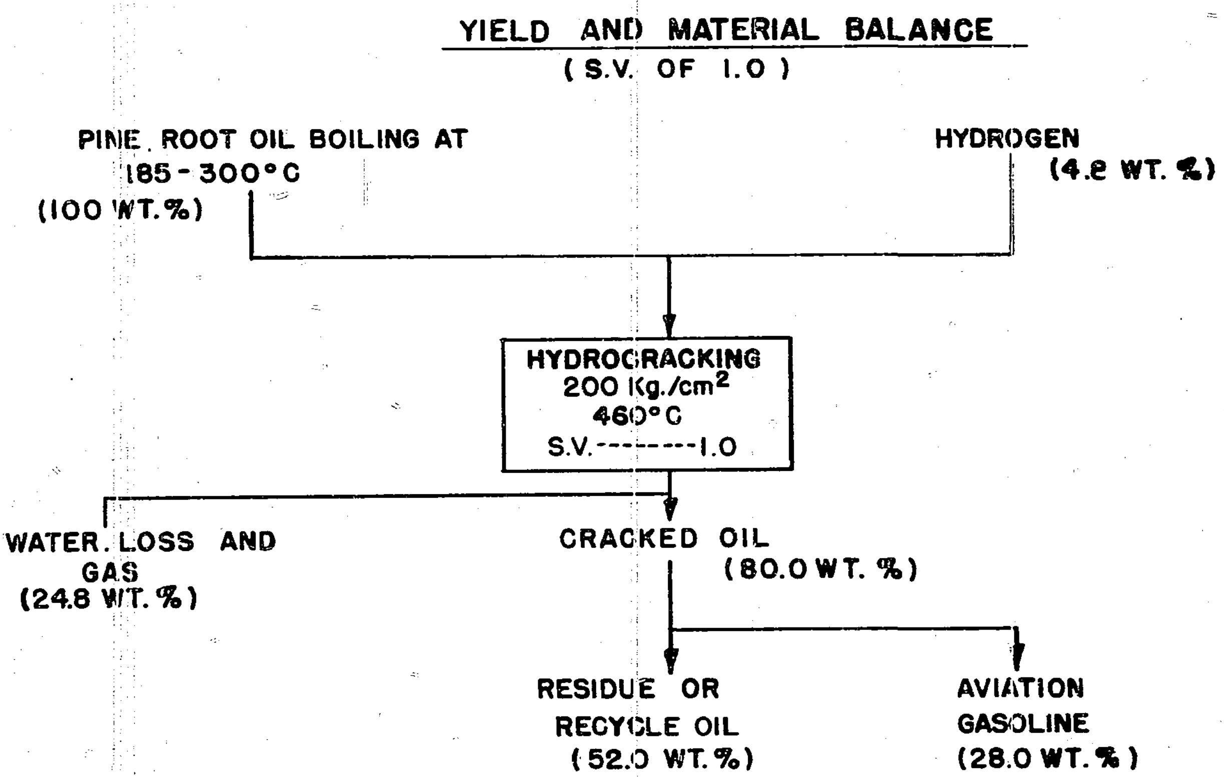


Figure 2(B)7
YIELD AND MATERIAL BALANCE
(S.V. of 1.0)

ENCLOSURE (B) 8

STUDIES ON THE MANUFACTURE OF AVIATION GASOLINE BY HIGH PRESSURE HYDROCRACKING OF PINE RESIN

by

CHEM. ENG. LT. COMDR. T. IJIMA
CHEM. ENG. LT. S. INABA

Research Period: May - Aug. 1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)8

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)8

SUMMARY

The object of this study was to find the optimum operating conditions for the manufacture of aviation gasoline, by high pressure hydro-cracking of pine resin. The semi-solid fraction of pine resin distilling above 300°C was hydro-cracked in an autoclave using Molybdenum Sulphide (MoS_3) catalyst and a 70% yield of cracked oil was obtained containing 40% of aviation gasoline with an octane number of 93-95 (0.15% lead).

I. INTRODUCTION

A. History of Project

Very recently, in response to the urgent demands of the war, pine resin was investigated as a source of aviation gasoline. No previous data were available on this subject. The key point of this research was to select proper reaction conditions for hydro-cracking the very stable pine resin, with high content of acidic matter (phenolic acid and abietic acid), so that high octane aviation gasoline could be obtained.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. S. INABA

II. DETAILED DESCRIPTION

A rotating autoclave of 2-5 liters capacity was used for these tests. Continuous pilot plant experiments were not made.

Properties of the raw pine resin are given below. The fraction boiling above 300°C. (about 50% of the raw pine resin), was used in these experiments. This fraction at room temperature was a hard solid of brownish color. Upon heating to 80-90°C, it became a viscous liquid.

Specific Gravity, d_4^{15}	1.023
Initial Boiling point (°C)	95
10%	155
20%	169
30%	228
40%	309
50%	318
60%	333
70%	346
80%	346
F.B.P.	354
Acid Value	122
Saponification Value	135

Physical and chemical properties of products are tabulated in Tables I(B)8 and II(B)8.

III. CONCLUSIONS

As the result of the autoclave tests, it was found that by high pressure hydrocracking of pine resin under the conditions of 200 kg/cm² hydrogen pressure, 430-450°C temperature, 2 hours reaction period, and using Molybdenum.

Sulphide catalyst, a good quality gasoline with 93-94 octane number (0.15% lead) could be produced in yield of 28%. This work was cut short due to the end of the war. It was planned to investigate this process on pilot plant scale, particularly to develop methods for handling the high viscosity melted pine resin in continuous operation. Further work to develop stronger and more active catalysts also was planned.

Table I(B)8
CONDITIONS OF REACTION AND PROPERTIES OF PRODUCTS
(Autoclave Test)

	Exp. No.	
	1	2
Catalyst	MoS_3	MoS_3
Reaction Conditions		
Reaction Temperature, °C	430	450
First Reaction Pressure, kg/cm^2	100	95
Final Reaction Pressure, kg/cm^2	65	63
Highest Reaction Pressure, kg/cm2	220	225
Reaction Time, hours	2	2
Products		
Absorbed Hydrogen wt. % of Raw Oil	4.3	4.6
Yield of Cracked Oil wt. % of Raw Oil	68	70
Water wt. % of Raw Oil	12.5	13.5
Acidic Matter vol. % in Cracked Oil	1.0	0.5
Specific Gravity of Cracked Oil	0.7869	0.7800
I. B. P. of Cracked Oil °C	39	38
10% Boiling Point of Cracked Oil °C	72	68
20% Boiling Point of Cracked Oil °C	94	89
30% Boiling Point of Cracked Oil °C	105	104
40% Boiling Point of Cracked Oil °C	118	116
50% Boiling Point of Cracked Oil °C	137	133
60% Boiling Point of Cracked Oil °C	153	150
70% Boiling Point of Cracked Oil °C	186	182
80% Boiling Point of Cracked Oil °C	199	192
90% Boiling Point of Cracked Oil °C	210	203
97% Boiling Point of Cracked Oil °C	233	220
Final Boiling Point of Cracked Oil °C	263	252
Total Distillate (vol %)	96	98
Residue (vol %)	2	1
Loss (vol %)	2	1
Residual Gas Composition (vol %)		
CO_2	0.2	0.3
O_2	0.3	0.4
C_nH_{2n}	0.9	0.5
CO	0.4	0.3
$C_nH_{2n}{}^{+2}$	16.5	17.5
H_2	78.2	76.2
N_2	3.5	4.8
n. (Carbon number)	0.9	0.6
Yield of Aviation Gasoline from Cracked Oil vol %	37	40

ENCLOSURE (B)8

Table II(B)8
PROPERTIES OF AVIATION GASOLINE
(Autoclave Test)

	Exp. No.	
	1	2
Reaction Temperature, °C	430	450
Specific Gravity D_4^{15}	0.7778	0.7614
Acidic Substance in Aviation Gasoline, vol. %	0.2	0
Fractional Distillation, °C		
Initial Boiling Point	42	33.4
10% Boiling Point	84	63.8
20% Boiling Point	94	80.2
30% Boiling Point	101	97.4
40% Boiling Point	108	105.6
50% Boiling Point	110.4	108.6
60% Boiling Point	120.5	118.5
70% Boiling Point	132	130.8
80% Boiling Point	147	147
90% Boiling Point	160	162
97% Boiling Point	170.4	168.5
Final Boiling Point	172.5	171.5
Total Distillate vol. %	95	98
Residue	3	1
Loss	2	1
Composition vol. %		
Unsaturated Hydrocarbon	3.0	0
Aromatic Hydrocarbon	21.3	24
Naphthenic Hydrocarbon	24.3	30.4
Paraffinic Hydrocarbon	51.4	45.6
Aniline Point	60.7	1.2
Octane Number		
Clear	78.0	79.0
With 0.15% of Lead	93.6	94.2

ENCLOSURE (B) 9

STUDIES ON THE COMPOSITION OF PYROLIGNEOUS LIQUOR AND ITS USES

by

CHEM. ENG. LIEUT. SAKOTA

Research Period: 1944-1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)9

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)9

SUMMARY

The pyroligneous liquor obtained by dry-distillation of pine roots was found to be composed of 4% organic acids, (mostly acetic acid) and mixed ketones. The acidic substances were precipitated as Ca-salts and subjected to dry distillation. The ketone oil thus obtained was 0.06% by vol. of the pine roots and had an octane value of 97 clear, and above 100 with 0.15% lead.

I. INTRODUCTION

A. History of Project

From August 1944 to end of war, research was done on the pyroligneous liquor obtained in yield of 30-50% from the dry distillation of pine roots. This material contains small amounts of acetone and methanol, but insufficient to justify recovery of these compounds. Besides these substances, the pyroligneous liquor contains 4% of organic acids, consisting mostly of acetic acid with some propionic; butyric and other acid homologues. These acid substances were known to be utilized in France for the preparation of "ketone oil".

B. Key Research Personnel Working on Project.

Chem.Eng. Commander H. FUJIMOTO
Chem.Eng. Lieutenant N. SAKOTA

II. DETAILED DESCRIPTION

A. Test Apparatus and Procedure

100 l. of concentrated pyroligneous liquor (d_4^{15} 1.03) were neutralized with Ca-hydroxide, 5% in excess, and filtered. The filtrate was concentrated and evaporated to dryness in open direct-fired steel evaporation dishes, 50 kg of Ca-cake was then heated at 370° for 8 hr. in the apparatus, shown in Figure 1(B)9, which contains 5 iron dishes. The distillate was then rectified several times to separate water from the ketone oil.

B. Experimental Results

An analysis of the pyroligneous liquor from dry distillation of pine roots is given in Table I(B)9. The crude Ca-salt cake was composed of Ca-acetate 30-40%, tarry matter above 10%, and water 5-10%. The tarry matter had a density of 0.780. Properties of the ketone oil obtained by several distillations of this tarry matter are as follows:

Sp. Gr. d_4^{15}	0.7804
Aldehyde(%)	0.01
Acid value	0
Distillation (°C)	
I.B.P.	52
10%	54
20%	55
30%	56
40%	58
50%	68
60%	72
70%	87

ENCLOSURE (B)9

80%	95
90%	107
97%	120
Dry point	135
Octane No. Clear	97
Octane No. 15% Pb	100

A material balance is given in Figure 2(B)9. Preliminary results on analysis of the ketone oil indicated the following approximate composition.

Acetone	50%
Methyl-ethyl-ketone	10%
Higher ketones	20%
Balance	10%
Total	100%

III. CONCLUSIONS

The pyroligneous liquor from pine roots was composed mostly of organic acids of the fatty series, with some ketones and methanol. The organic acids, separated as Ca-salts, were subjected to dry distillation, and the tar, or so-called ketone oil, showed an octane value of 97 clear, and above 100 with lead.

Table I(B)9
DISTILLATION AND PROPERTIES OF PYROLIGNEOUS LIQUOR

Time	D. Distil'n. Temp. °C.		Properties of Pyroligneous Liquor				
	Oven I	Oven II	Sp. Gr. d_{15}^{15}	Org. Acid as Acetic Acid (%)	Acetone (%)	Methanol (%)	Dissolved Tar (%)
07 20							
10 20	70	95	1,010	0.87	0.21	0.48	2.6
11 20	70	95	1,012	1.08	0.21	0,67	4.0
12 20	110	115	1,015	1.97	0.20	0.76	3.8
13 20	185	145	1,017	4.42	0.21	1.03	4.0
14 20	260	200	1,018	4.27	0.21	1.02	7.5
15 20	265	325	1,032	6.27	0.19	1.01	8.0

ENCLOSURE (B)9

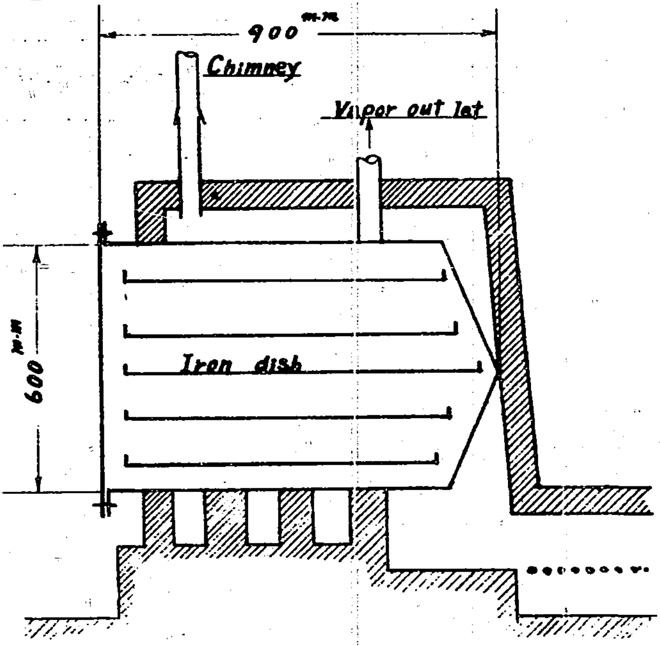


Figure 1(B)9

APPARATUS FOR CARBONIZATION OF CA-ACETATE

ENCLOSURE (B)9

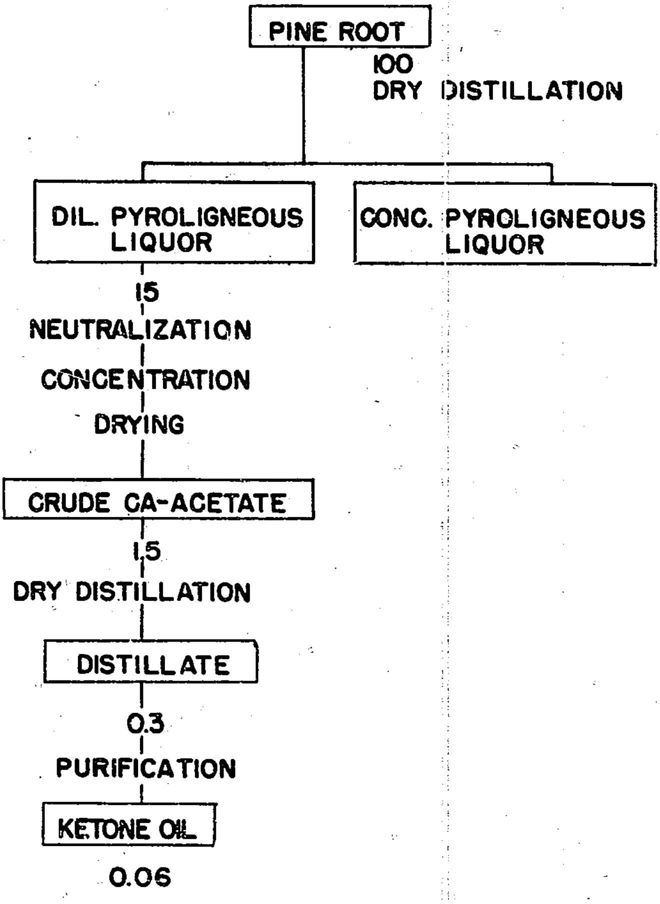


Figure 2(B)9
MATERIAL BALANCE
(yields in wt.%)

ENCLOSURE (B) 10

ENGINE TEST OF AVIATION GASOLINE PRODUCED FROM THE UNTREATED PINE ROOT OIL

by

CHEM. ENG. LT. COMDR. T. NAKAYAMA

Research Period: 1945

Prepared for and Reviewed with Author by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)10

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)10

SUMMARY

Distillate of crude pine root oil, the distillation range under 185°C was tested in Kinsei single-cylinder test engine as to whether it could be used as aviation gasoline without any treatment such as hydro- or catalytic cracking. The volatility of the sample was very low, and the content of gummy substance was so much that it could hardly have been used in carburetors, and so it was decided to test it blended with ethyl alcohol. The essential results were as follows:

1. Maximum allowable boosts of the sample are shown in Table I(B)10.

2. Only Sample No. 1 passed the endurance test of about 17 hours, but the condition was not sufficiently satisfactory to permit its use in first class aviation engines.

3. Although the gum content of Sample No. 1 was over 350 mg/cc, no intake value or ring sticking occurred during the endurance test.

I. INTRODUCTION

A. History of Project

These experiments were commenced in Feb. 1945 and were not completed. Aviation gasoline obtained by the catalytic or hydro-cracking of the distillate of pine root oil up to 300°C was sent to the First Naval Technical Depot at YOKOSUKA, and tested in full scale aviation engines of the first class, and found to give the same performance as the ordinary aviation fuel of the same octane rating. It was requested that the crude gasoline produced from the pine root oil be examined, by properties, single-cylinder engine tests.

B. Key Research Personnel Working on Project

Chem. Eng. Comdr. K. NAKATA
Chem. Eng. Lieut. Comdr. T. NAKAYAMA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus and Test Procedure

This is the same as that described in "Engine test of alcohol as aviation fuel".

B. Experimental Results

The properties of the distillate of pine root oil up to 185°C were as follows:

ENCLOSURE (B)10

Octane Rating	70
Distillation Temperature	(°C)
First drop	100°C
10% point	140
50% point	160
90% point	170
97% point	180

It had very poor antiknock value and volatility, so it could not be used in aircraft engines. To improve these properties, ethyl alcohol was blended in the fuel. At first, 80% ethyl alcohol blended fuel was tested. The properties of the mixture of alcohol and the distillate of pine oil were as follows:

Composition of misture (by volume): Alcohol 80% and Distillate 20%
Octane Rating: 85 (C.F.R. Motor Method)
Gum Content: 350 mg/100cc of mixture
Distillation Temperature:

First drop	75°C
10% point	78°C
50% point	78°C
90% point	170°C
97% point	180°C

This blended fuel was tested by Kinsei single cylinder testing plant and the results were as shown in Table II(B)10.

This performance was almost equal to that of alcohol. Next, the effect of gum content was examined. An endurance test of about 15 hours was made under the following conditions: 2500 RPM, boost +150mm Hg, air fuel ratio 7--8 by weight, (fuel consumption 35-36 lit/hr) and about 50 horse power. After about 11 hours, the front ignition plug was found to be misfiring due to gum. Engine was stopped, the plug changed, and the test was continued until the prepared fuel was used up. After about 17 hours total running time, the test was stopped, and the interior of the engine was examined. No deposits were observed at the inlet valve, exhaust valve, spark plug, piston, piston ring etc., although the gum content was extraordinarily large compared with that of ordinary cracked gasoline. Next, the content of ethyl alcohol was reduced. Octane ratings of the mixtures of distillate 70%, alcohol 30%; and distillate 50%, alcohol 50%, were 75 and 80 respectively. Engine tests showed their maximum allowable boosts, -100mm Hg and ±0mm Hg respectively. Thus, these mixtures cannot be used as aviation fuel because of their poor antiknock properties.

III. CONCLUSIONS

Crude pine root oil itself cannot be used as aviation gasoline because of its poor volatility, low antiknock value, and tendency to form gum on spark plugs when the engine is operated for long periods of time at low temperature. If the crude pine root oil is added in small quantity (20% by volume) to ethyl alcohol, the blend can be used approximately the same as ethyl alcohol.

ENCLOSURE (B)10

Table I(B)10
MAXIMUM ALLOWABLE BOOSTS OF SAMPLE

Sample No.	Composition of Fuel (Vol %)		Max Allowable Boost
	Distillate of Pine Root Oil	Ethyl alcohol	
1	20	80	+ 300mm Hg
2	50	50	± 0mm Hg
3	70	30	-100mm Hg

Table II(B)10
TEST RESULTS

RPM	Boost (mm Hg)	Fuel Consumption (lit/hr)	hp	Cyl. Temp.	Exhaust Temp.
2200	300	43	70	180	640
		42		195	650
		41		210*	650

ENCLOSURE (B) 11

UTILITY TESTS OF PINE ROOT OIL

by

ENG. CAPTAIN T. KONDO
ENG. LT. COMDR. S. SOMA

Research Period:
From March - Aug. 1945

Prepared for and Reviewed with Authors by
the U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)11

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)11

SUMMARY

Aviation gasoline prepared from pine root oil by catalytic cracking or hydrocracking in the First Naval Fuel Depot showed no difference from gasoline No. 1 (see following page) in connection with engine performances, and starting and acceleration abilities. Although the gasoline produced by catalytic cracking was said to cause gum-swelling in the fuel line of engines, no trouble was actually encountered during the flight test period. Crude pine root oil with 50% of (by vol.) 99% alcohol caused a large amount of deposit in the fuel line, for instance, in the carburetor nozzle, acceleration pump, fuel pump, and filters. Moreover, its practical antiknock ability was under 87 octane gasoline and it was impossible to apply this gasoline to practical engines before the end of the war.

I. INTRODUCTION

A. History of Project

In March 1945, the treatment of pine root oil was completed in the First Naval Fuel Depot, and two kinds of samples were sent to the First Naval Technical Depot to examine their applicability by bench and flight-tests in practical engines. Results were obtained in April 1945. In May 1945, a sample of crude pine root oil with 50% of 99% alcohol was sent to the First Naval Technical Depot, and immediate investigations were made applying the bench tests of practical engines.

B. Key Research Personnel Working on Project

Eng. Capt. T. KONDO
Eng. Lieut. Comdr. S. SOMA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

Engines: HOMARE 20 type
Aeroplane: SHIDEN (fighter with HOMARE 20 type engine)

B. Test Procedures and Experimental Results

The two kinds of aviation gasoline produced from pine root oil by the First Naval Fuel Depot by catalytic cracking or hydrocracking had almost the same properties as the No. 1 gasoline. HOMARE 20 type engine was operated with these fuels on a performance test bench utilizing a Froude dynamometer. Maximum allowable boost pressures and minimum economical consumptions were examined and the following data obtained (from memory):

Maximum allowable boost pressures of the two samples showed the same results as the gasoline No. 1. Although minimum economical consumptions in grams/hp-hour of the sample by catalytic cracking showed somewhat greater results than gasoline No. 1 specific gravity of the former was somewhat heavier than that of the latter, thus actually giving the same consumptions in lit/hp-hour. These performances were ascertained by flight tests of the SHIDEN airplane. Although it was considered that the sample from catalytic cracking would give gum-swelling trouble in the fuel line (BUNA-N) of engines, because of the large percentage of aromatic compounds, no actual trouble was encountered during the bench and flight test period.

There was no trouble with starting and accelerating abilities of the engines. Also no gum troubles were encountered in practical service.

Crude pine root oil with 50% of 99% alcohol caused engine trouble due to the large amount of deposits in the fuel line; i.e. the carburetor nozzle, acceleration pump, fuel pump, and filters. Moreover, its practical anti-knock ability was lower than that of 87 octane gasoline, rendering its use for practical combat aeroplanes unsuitable.

III. CONCLUSIONS

The two samples of gasoline prepared from pine root oil (one by catalytic cracking and the other by hydrocracking) were found suitable as substitutes for gasoline No. 1.

Table I(B)11
PROPERTIES OF AVIATION GASOLINES FROM PINE ROOT OIL

	Sample from Catalytic Cracking	Sample from Hydrocracking	No. 1 Gasoline
First Drop	45.5°C	48°C	60°C max
10% pt	76	85	90 max
50	115	110	115 max
90	149	155	160 max
97	167	170	170 max
Sum of 10,50,90%	over 260°C	over 260°C	260°C min
Leaded	0.15%	0.13%	0.15% max
Vapour Pressure	0.6 kg/cm^2	0.4 kg/cm^2	under 0.6 kg/cm^2
Specific Gravity	0.78	0.74	0.73 - 0.74

Table II(B)11
PERFORMANCE TEST OF AVIATION GASOLINES FROM PINE ROOT OIL

	Sample from Catalytic Cracking	Sample from Hydrocracking	No. 1 Gasoline
Allowable Max	(1st speed) +500mm/Hg	(1st speed) +500mm/Hg	(1st speed) +500mm/Hg
Boost Pressure	(2nd speed) +350mm/Hg	(2nd speed) +350mm/Hg	(2nd speed) +350mm/Hg
at 3000 RPM	over 125mm/Hg with supplementary fuel		
Min Economical Consumptions at 2000 RPM -200mm/Hg	220 gm/hp-hour	210	210

RESTRICTED

ENCLOSURE (C)

ENCLOSURE (C)

PINE ROOT OILS

Reference NavTechJap Document No. ND. 26-0010, ATIS No. 4581

Prepared for the U. S. Naval Technical Mission
to Japan

December 1945

ENCLOSURE (C)

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ENCLOSURE (C)

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

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.

ENCLOSURE (C)

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

ENCLOSURE (C)

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 DISTILLATION 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 manage-

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ment 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.

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 1 1/3 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 apparatus for the next distillation, and distillation is stopped after 10-11 hours. Therefore ideal operations cannot be realized.

ENCLOSURE (C)

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 ~~ears~~ 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).

ENCLOSURE (C)

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

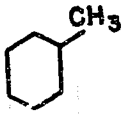
Crude pine root oil obtained from "Kuromatsu" was fractionated, and after treating with sufficient alkali the constituents were examined.

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

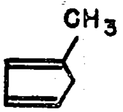
Note: * Sign indicates main constituents.

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

* Toluene (B.P. 110°C)



* Sylvene



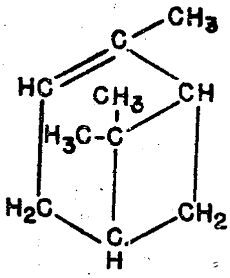
Sylene Furan Furfural

Diacetyl $(CH_3CO)_2$

Acetylpropionyl $(CH_3CO.C_2H_5CO)$

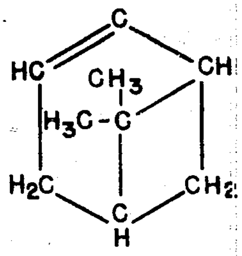
b. Terpene fraction (150-170°C) (40-70%)

* 1-a-Pinene (B.P. 155-156°C)



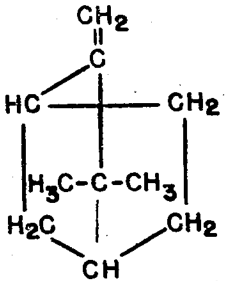
ENCLOSURE (C)

* Limonene and Dipentene (B.P. 175°C)

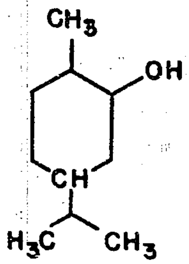


* Camphene

(M.P. 50°C)

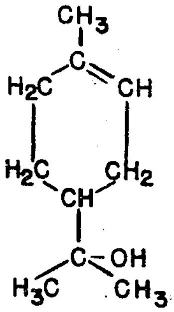


p-Thymol



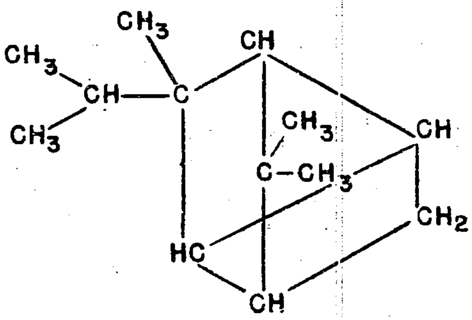
c. Terpenic alcohol fraction (200-230°C) (small amount

* 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).

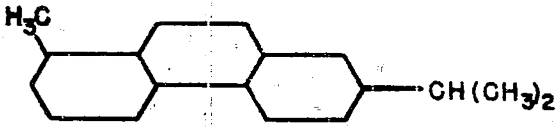


ENCLOSURE (C)

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

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

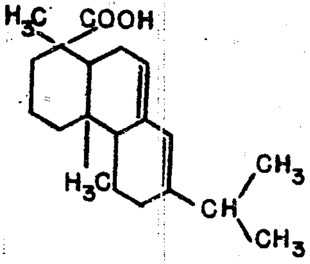
* Retene (M.P. 98°C), constituent of paraffinic crystal



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.

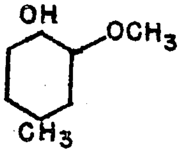
Acetaldehyde CH_3CHO and acetone $CH_3.O.CH_3$ are probably present.

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

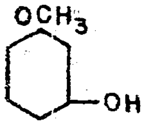
Formic acid (B.P. 100.6°C)
Propionic acid C_2H_5COOH (B.P. 140°C)
Isobutyric acid $(CH_3)_2CH.COOH$ (B.P. 154°C)
Valeric acid C_4H_9 COOH (B.P. 185°C)
Capronic acid $C_5H_{11}COOH$ (B.P. 205°C)
and other higher carboxylic acids.

(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,

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

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

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 (Prioa 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).

ENCLOSURE (C)

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	2884,000	3750,000	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
Oita	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

	Temperature (°C)							Distillate from Tar-Separator								Distillate from Cooler									Fuel	
Time (o'clock)	Center of Retort		Separator		Cooler Inlet		Cooler Water	Sum (kg)	Oil (cc)	Sum (lit)	Tar (cc)	Sum (lit)	Pyrolig. (cc)	S.G.	Sum (lit)	Sum (kg)	Oil (cc)	S.G.	Sum (lit)	Tar (cc)	Sum (lit)	Pyrolig. (cc)	S.G.	Sum (lit)	R (kg)	L (kg)
	R	L	R	L	R	L																				
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	88	93		88		8.4	2100	2.1			6300	1.010	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	94	98	95	65	89		4.4/20.5			130	0.13	4270		17.27	9/10.5	2860	0.8944	2.99	100	0.100	6040		8.435		
1130	97	99	95	95	660	95		3.0/23.5			70	0.2	2930	1.007	20.2	9.8/20.3	1600	0.8982	4.59	70	0.170	8130	1.015	16.565	10	
1200	105	95	96	95	70	98	14.6	2.8/26.3					2800		23.0	16.5/36.8	3050	0.8985	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	0.9397	11.12			15.320	1.008	45.335		
1300	143	161	99	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	0.9692	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	1.0142	29.6			16.450		87.555		
1430	205	257	110	95	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	95	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	153	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	56	46		20.0	1.0/83.9			1000	52.58				1.5/179.8	350		45.20			1.150		125.455		
1700	300		70		40		17.0																			
1730																									Sum 60	50

Notes:

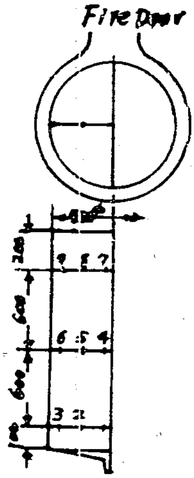
0.830: First Drop of Pyroligneous Liq. from Tar Separator
0.940: First Drop of Tar from Tar-Separator
1025: First Drop of Oil from Cooler
1220: Non-Condensed Gas is beginning to burn at Fire Door

Feed: Pine-Root (water-content .... 17%)
Charged - Right .... 253 kg
Left .... 248 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.

Table VIII(C)
EXPERIMENTS OF PINE TRUNK DRY DISTILLATION

No. of Experiment	Weight of Materials (kg)	Water Content (1) (%)	Yield			Yield to Weight of Material (%)	Fuel				Operation Time (hrs)
							Weight Consumed			Consumption Ratio to wt. of Material	
			Tar (1)	Crude Oil (1)	Total (1)		Fire-wood (kg)	Char-coal (kg)	Total (kg)		
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	15.5
	Pine	10.9
	Japanese cypress	11.6
Twigs	Cyptomeria	3.55
	Pine	6.11
	Japanese cypress	2.88

ENCLOSURE (C)

Table XI(C)
CATALYTIC DRY DISTILLATION OF VARIOUS TREES

Trees	Crude Oil			Distilled Liquid		Charcoal gm/100 gm
	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	
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 arbervitae)*	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

Experiment 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)	Substitute 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)

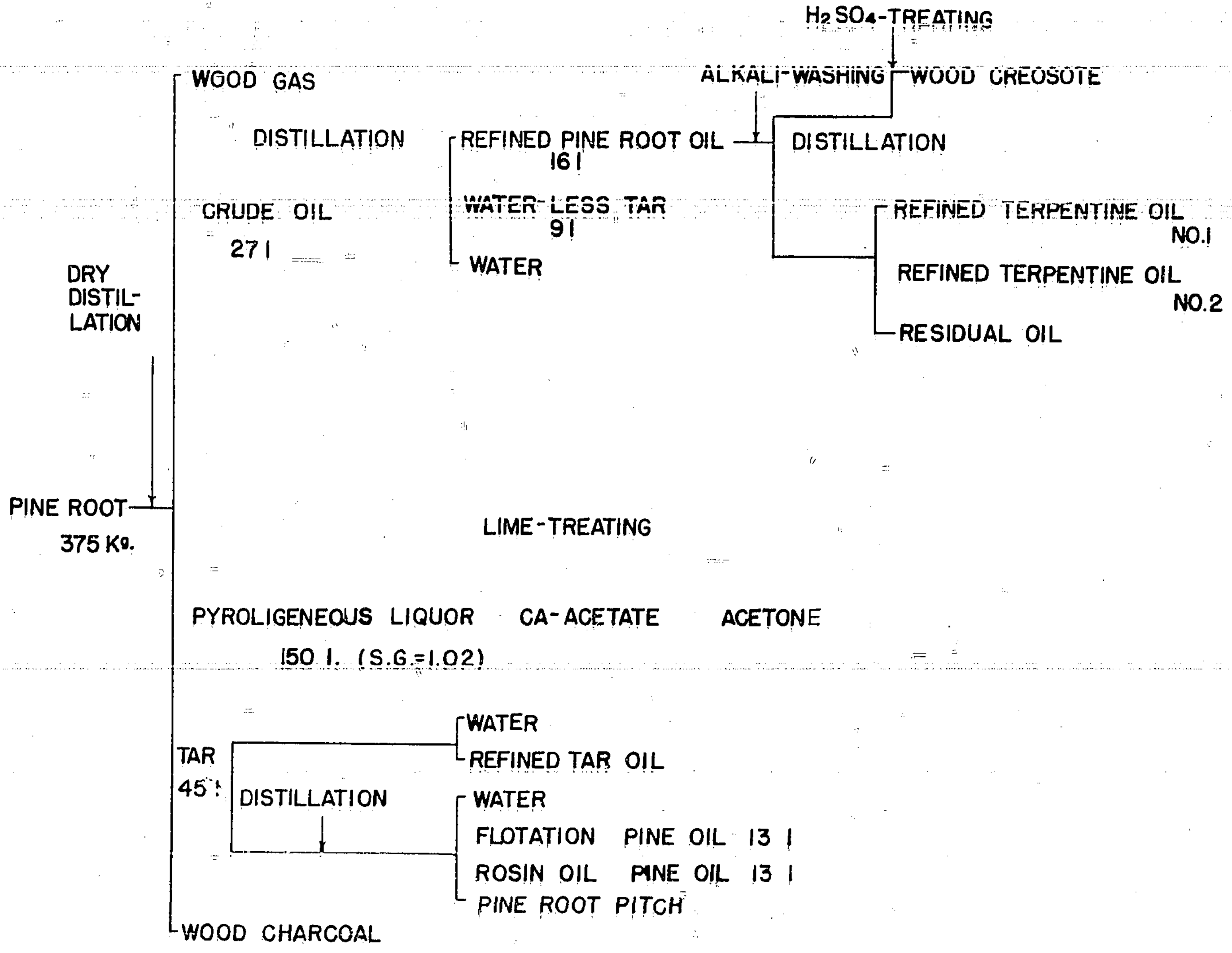


Figure 1(C)

FLOW SHEET OF REFINING PINE ROOT OIL

Vertical Retort

ENCLOSURE (C)

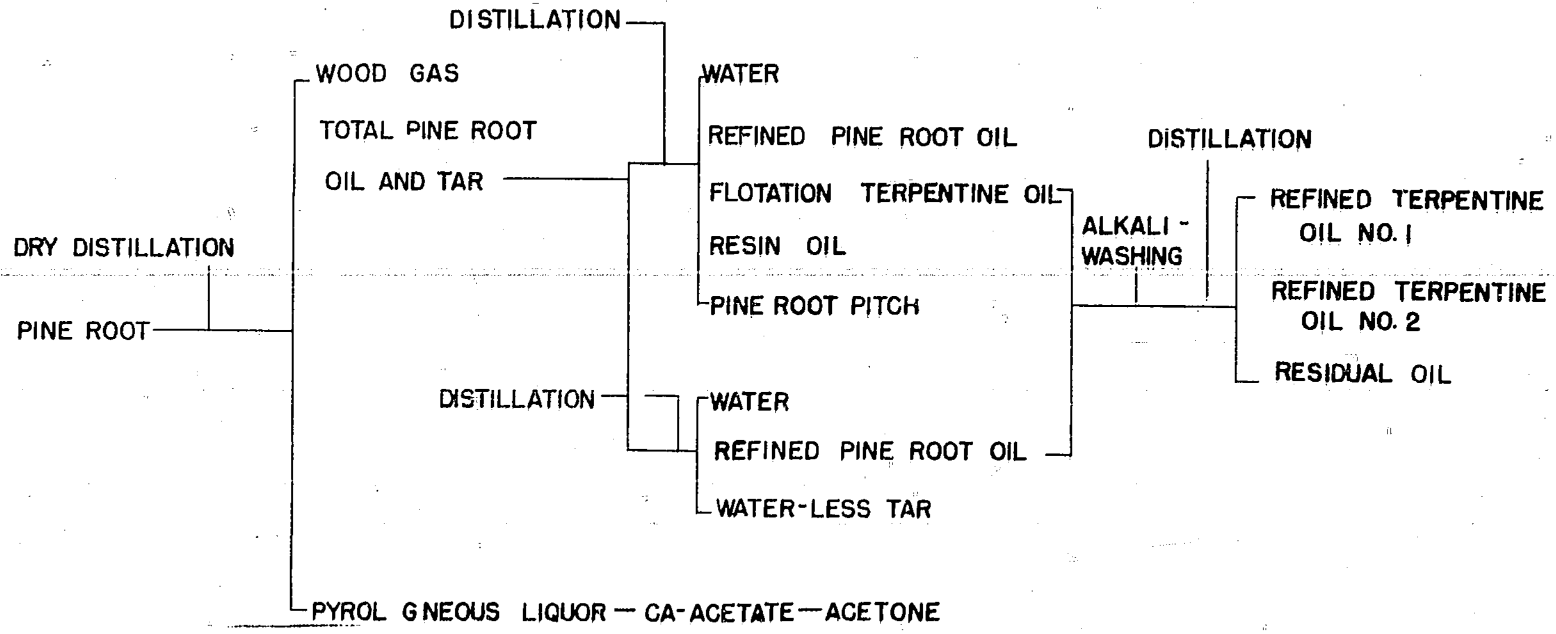


Figure 2(C)
FLOW SHEET OF REFINING PINE ROOT OIL
Horizontal Retort

ENCLOSURE (C)

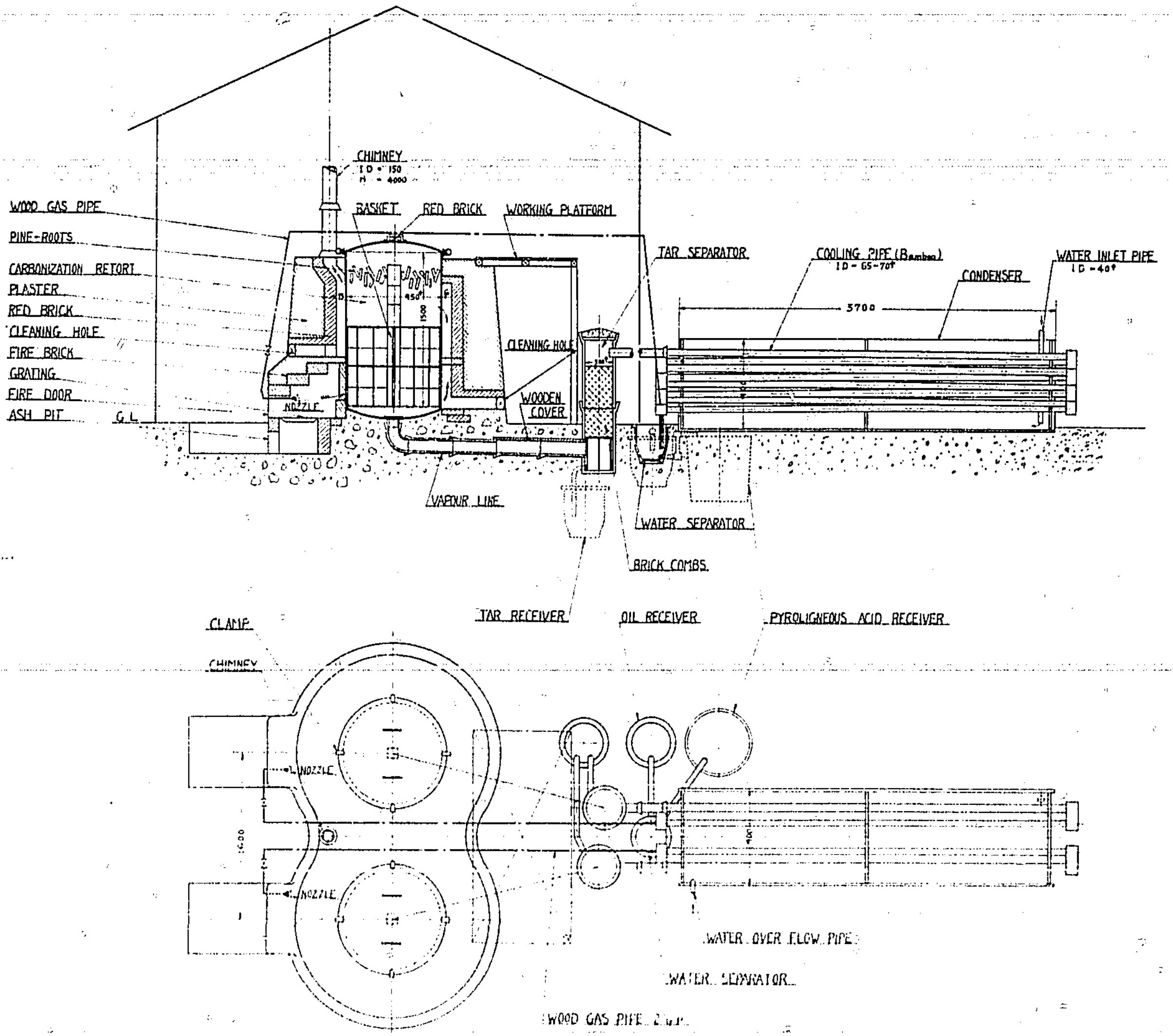


Figure 3(C)
GENERAL ARRANGEMENT OF CARBONIZATION APPARATUS OF PINE-ROOT
Daily Capacity 750kg/1 set

ENCLOSURE (C)

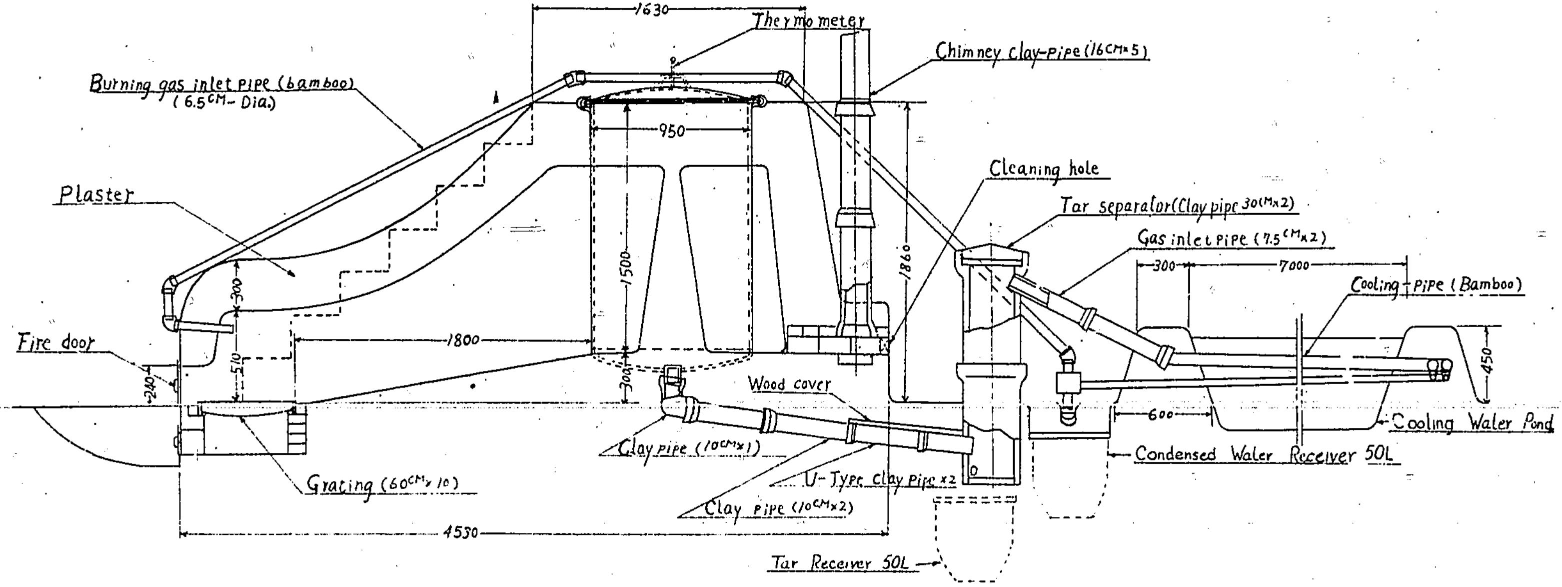


Figure 4(C)

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

Daily Capacity 375kg/1 set

ENCLOSURE (C)

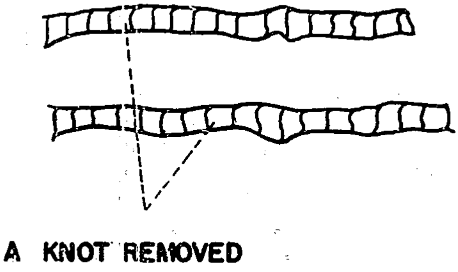


Figure 5(C)
INCLINED BAMBOO COOLING TUBE

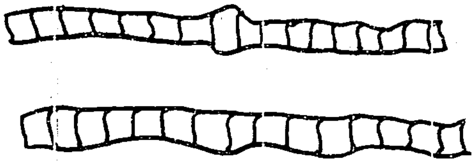


Figure 6(C)
HORIZONTAL BAMBOO COOLING TUBE

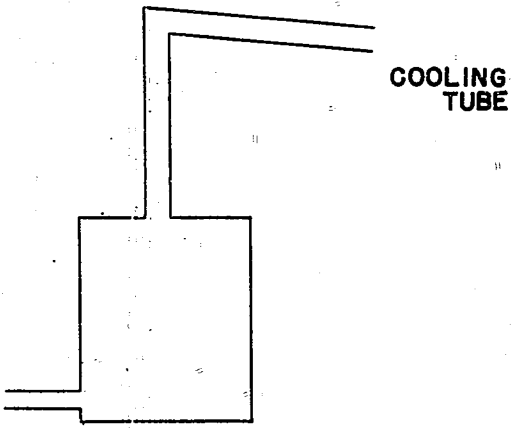


Figure 7(C)
VERTICAL APPARATUS

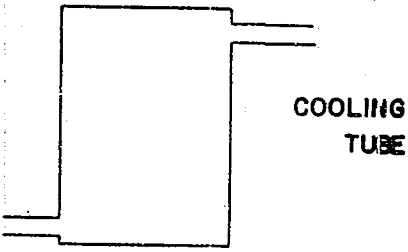


Figure 8(C)
HORIZONTAL APPARATUS

ENCLOSURE (C)

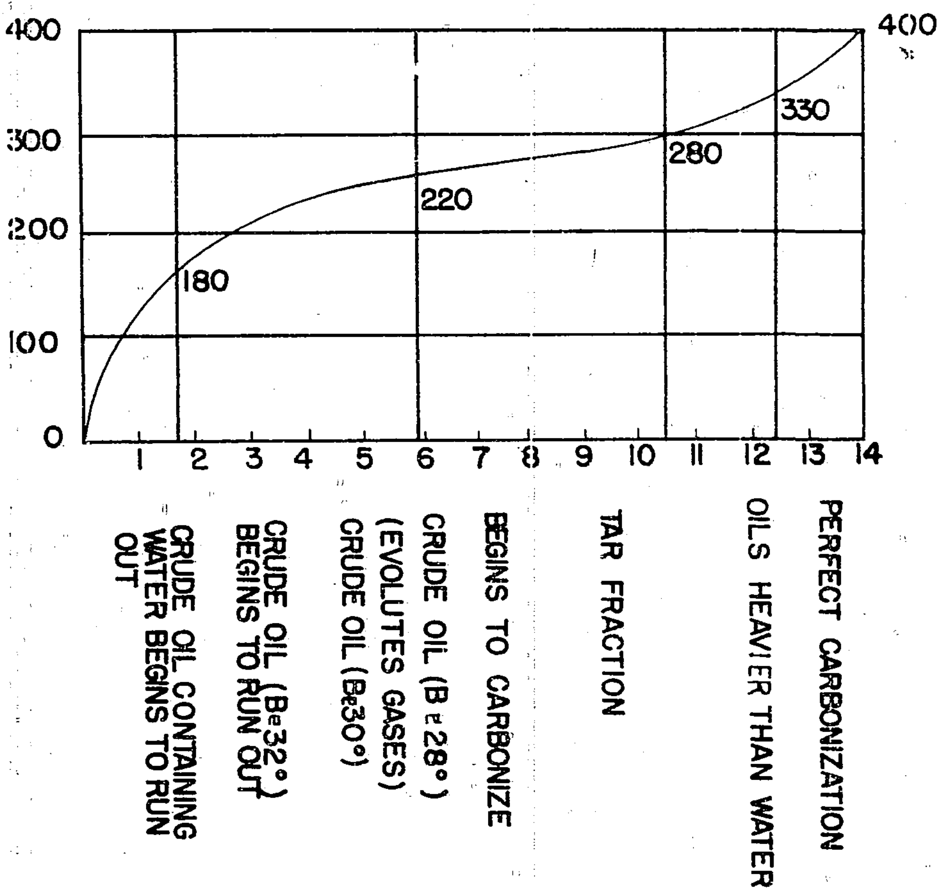


Figure 9(C)
PROGRESS OF DISTILLATION

ENCLOSURE (C)

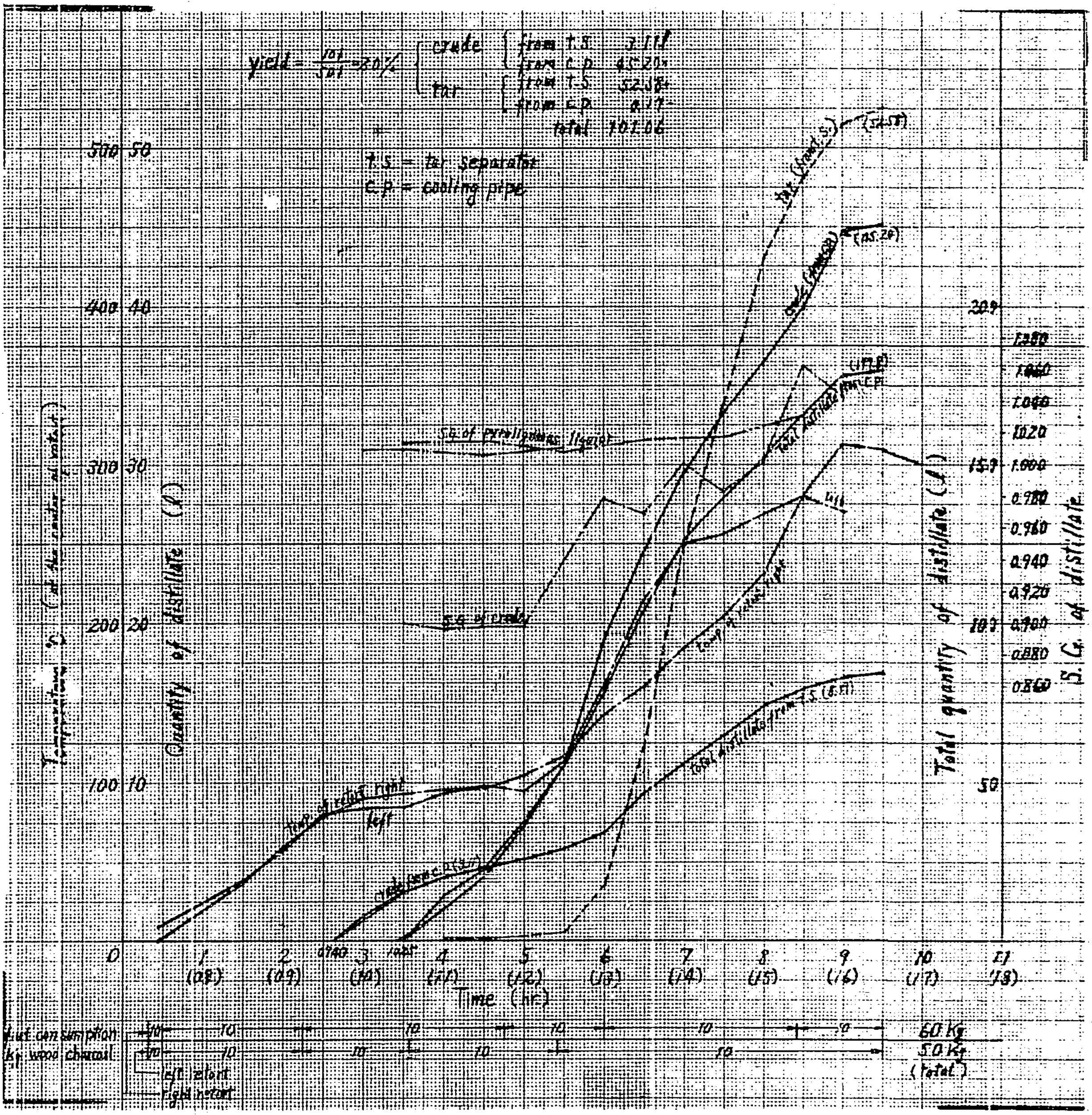


Figure 10(C)

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)

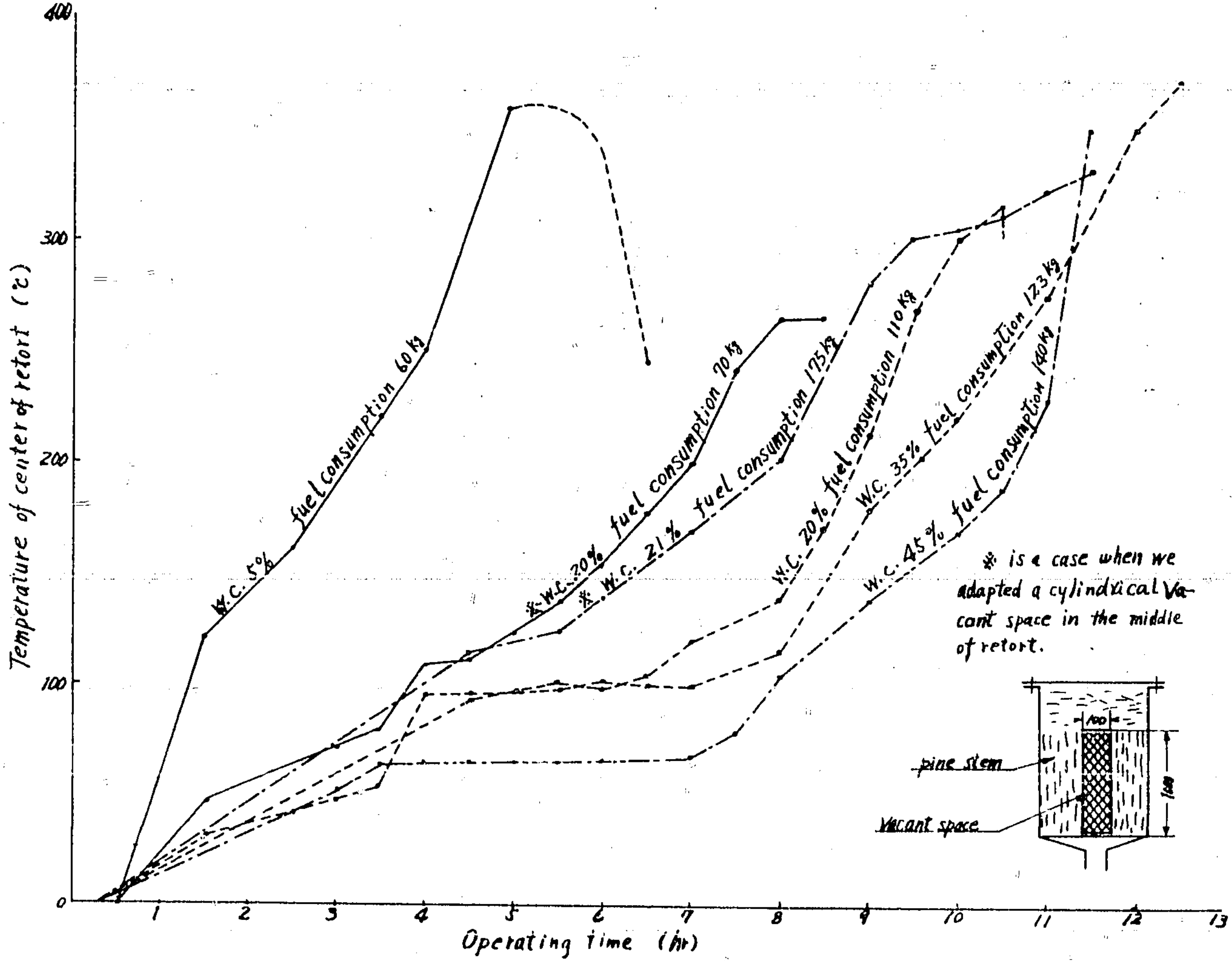


Figure 11(C)
RELATION BETWEEN THE TEMPERATURE OF THE CENTER OF RETORT AND THE WATER CONTENT OF PACKED PINE STEM
A Type Apparatus

ENCLOSURE (C)

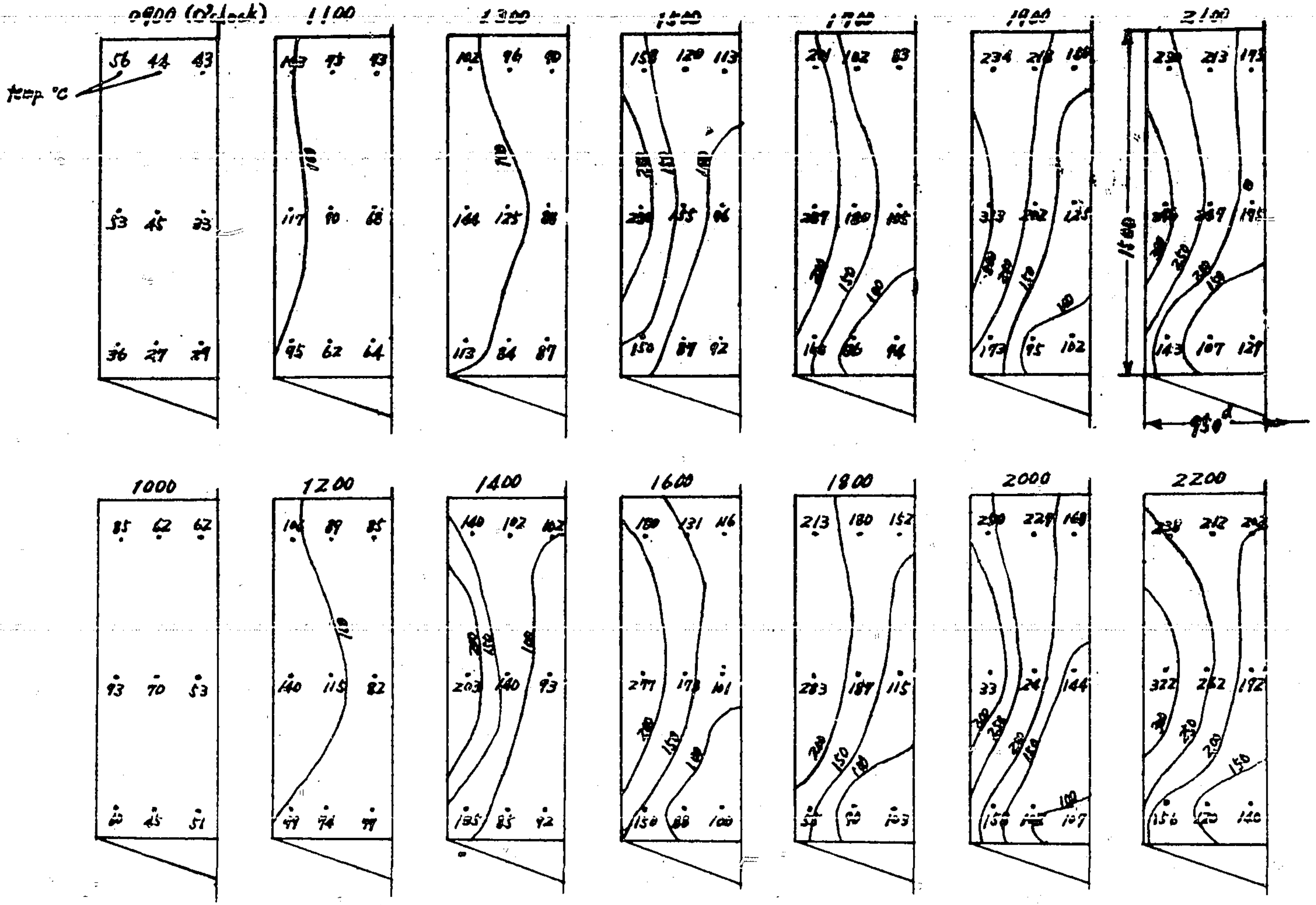


Figure 12(C)
THE CHANGE OF THE TEMPERATURE DISTRIBUTION IN THE RETORT (USING THE PINE STEM)
(A Type Retort)

ENCLOSURE (C)

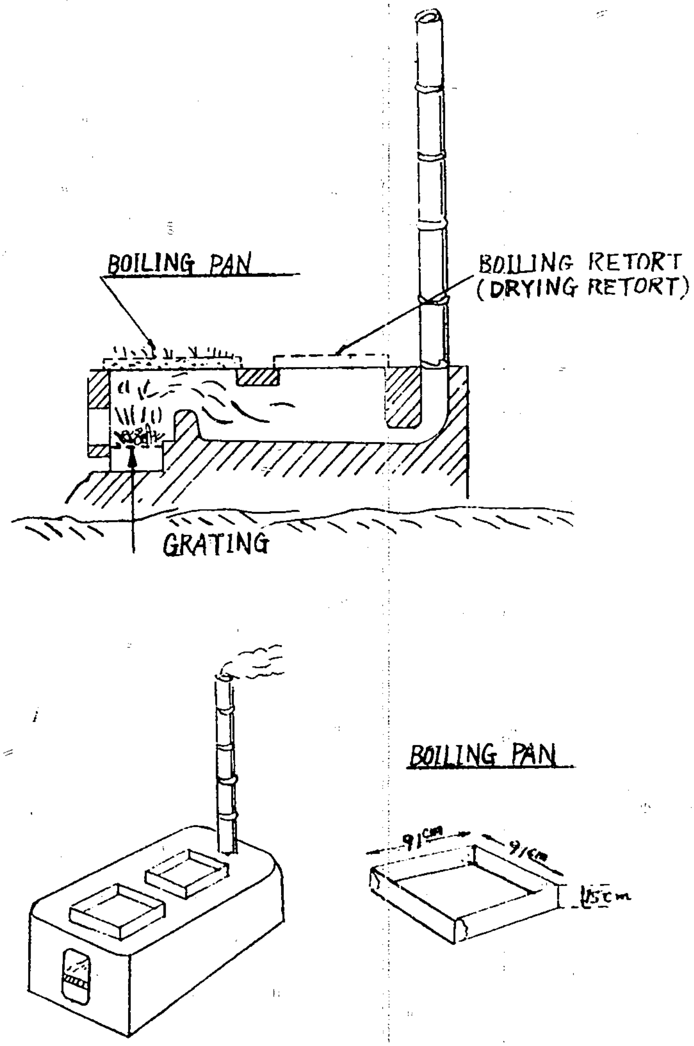


Figure 13(C)
BOILING PAN OF PYROLIGNEOUS LIQUOR

ENCLOSURE (C)

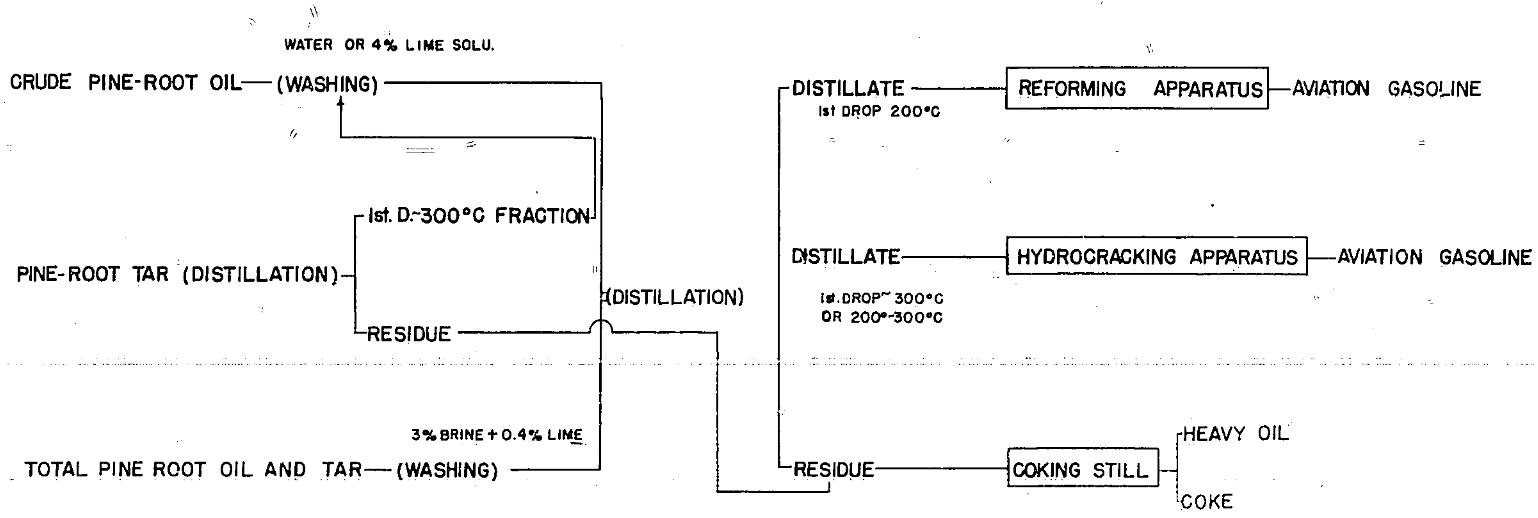


Figure 14(C)
PRODUCTS FROM PINE ROOT OIL (FLOWSHEET)

ENCLOSURE (C)

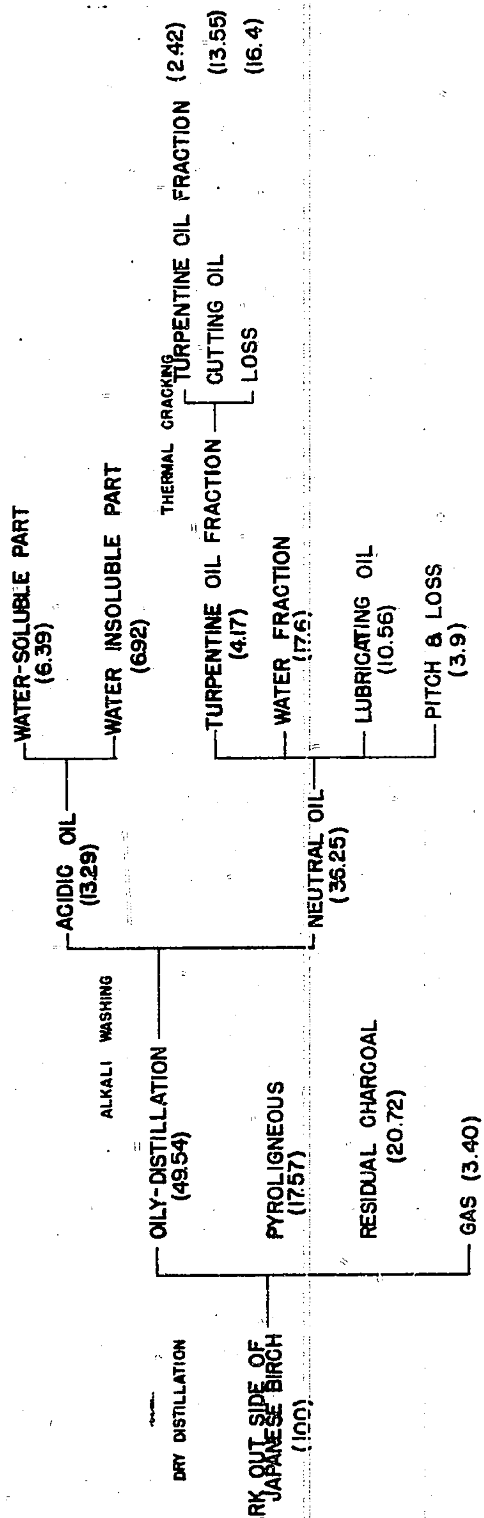


Figure 15(C)
PRODUCTS FROM JAPANESE BIRCH (FLOWSHEET)

RESTRICTED

ENCLOSURE (D)

ENCLOSURE (D)

MITSUBISHI RESIN-OIL FACTORY

SHIMABARA, KYUSHU

ENCLOSURE (D)

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ENCLOSURE (D)

SUMMARY

The Mitsubishi Resin-oil Factory, SHIMABARA, Kyushu, was visited by the Petroleum Team of the U. S. Naval Technical Mission to Japan on 18 October, 1945. Data obtained, including information concerning management details, equipment, details of manufacture, and type of products, are presented herewith.

This plant is typical of units set up by the Japanese government throughout Japan for the purpose of preparing pine root oil by the dry distillation of pine roots. This oil has been used as an emergency fuel substitute for various types of gasoline engines.

I. INTRODUCTION

The Mitsubishi Resin-Oil Factory is located in SHIMABARA, Nagasaki Prefecture, Kyushu. The plant is located about one mile west of SHIMABARA on the road to UNZEN. Mr. ISHIGARA, the Business Manager, was interviewed by the Petroleum Team on 18 October 1945 and assisted in supplying the information presented herewith.

II. HISTORY AND ORGANIZATION

The Mitsubishi Resin-Oil Factory at SHIMABARA was established at the request of the Japanese government in June 1945. The plant is typical of a large group of such plants which were set up throughout Japan during 1945. This factory is a unit of Mitsubishi Denki in NAGASAKI and is directly controlled by the parent organization. It was originally designed to manufacture tar paint and solvents for insulating materials.

Details concerning the evaluation of the property and equipment are presented in Appendix I.

III. PERSONNEL

The Director of the factory is Mr. Kuichi ISHIGURO. There a total of 55 employees in the organization, 34 of whom are shop workers and the remainder comprise the office force.

IV. DESCRIPTION OF PROCESS

Pine roots are dry distilled by heating in metal retorts. After distillation the charcoal is used as fuel for heating the next batch of roots. The products of the distillation are pine tar and crude oil. The tar is collected in metal containers attached to the retort outlets and the oil is condensed by circulating in metal pipes through a large cooking tank.

The tar and the oil are then distilled in separate units. The oil is fractionated and one cut is prepared which has a boiling range of 120°C-230°C. This cut is called "Turpentine Number 1". The remaining oil is mixed with the tar and distilled off by simple retort-type, distillation. The product is called "Turpentine Number 2" and has a boiling range of 230°C - 380°C. Both oils are neutralized to a phenolphthalein end point with a 5% caustic soda solution. The residue is pitch for which there is not useful application at present.

At the time of the inspection of this plant the fractionating column was not available for inspection, since it had been corroded beyond repair. Scarity of materials had prohibited the construction of a new unit.

ENCLOSURE (D)

V. PRODUCTS AND PRODUCTION CAPACITY

The principal products are "Turpentine No. 1" and "Turpentine No. 2". Pitch is a by-product of the process. Intermediates of interest are the crude oil and pine tar which are obtained during the process. Pint samples of each grade of turpentine and the two intermediates, and a sample of pitch were obtained and are being sent to the Ordnance Investigating Laboratory, Indianhead, Md. for forwarding to the Naval Research Laboratory, Anacostia, Md. (NavTechJap Serial No. JE-26-0007, Items 1-5)

The normal monthly production of the plant is 40 drums of No. 1, 60 drums of No. 2, and 2 tons of pitch. At the present time none of the material has been shipped and the entire production is on hand. The stock on hand is 151 drums of No. 1, 58 drums of No. 2, and approxmately 10 tons of pitch.

VI. PRODUCT APPLICATIONS

"Turpentine No. 1" is used as a solvent, or mixed with alcohol, as a fuel for gasoline engines. "Turpentine No. 2" may also be mixed with alcohol and used as an automotive gasoline engine fuel or, without mixing, it may be used as fuel oil for small craft. At the present time there is no application for the pitch formed during the distillation process.

A simplified material flow diagram, showing proposed applications of the various products is presented in Appendix II. This diagram describes proposed plans and has not yet been incorporated in the actual operation of the plant.

VII. CONCLUSIONS

This plant is typical of many similar units which have been set up by the Japanese government, altho the fractionating temperatures differ somewhat from those established by the Japanese Navy. As such it is of interest since the existence of these plants indicates the acute need for any material which could serve as a gasoline engine fuel.

ENCLOSURE (D).

APPENDIX I

OUTLINE OF MITSUBISHI DENKI (SHIMABARA KOJO)

(As submitted to the U. S. Naval Technical
Mission to Japan)

1. Name - Mitsubishi Denki (Shimabara Kojo.)
2. Director - Kuichi ISHIGURO
3. Factory Management - The plant is a branch of Mitsubishi Denki in NAGASAKI. The parent organization controls the finance, processes, raw materials, and products of subject plant.
4. Date Established - June 1945
5. Cost of Land, Buildings and Equipment - 375,000 yen
6. Products and Product Applications
    - a. Turpentine No. 1 - Fuel, Solvent
    - b. Turpentine No. 2 - Marine fuel
    - c. Pitch - (By product, no application)
7. Monthly Production Capacity

a. Turpentine No. 1	40 drums (2000 gal.)
b. Turpentine No. 2	60 drums (3000 gal.)
c. Pitch	2 tons

8. Pine Root in Stock

a. Turpentine No. 1	151 drums
b. Turpentine No. 2	58 drums
c. Pitch	10 tons

9. Intermediate Products in Stock

a. Crude Pine Root Oil	129 drums
b. Pine Root Tar	539 drums

10. Employees - 55

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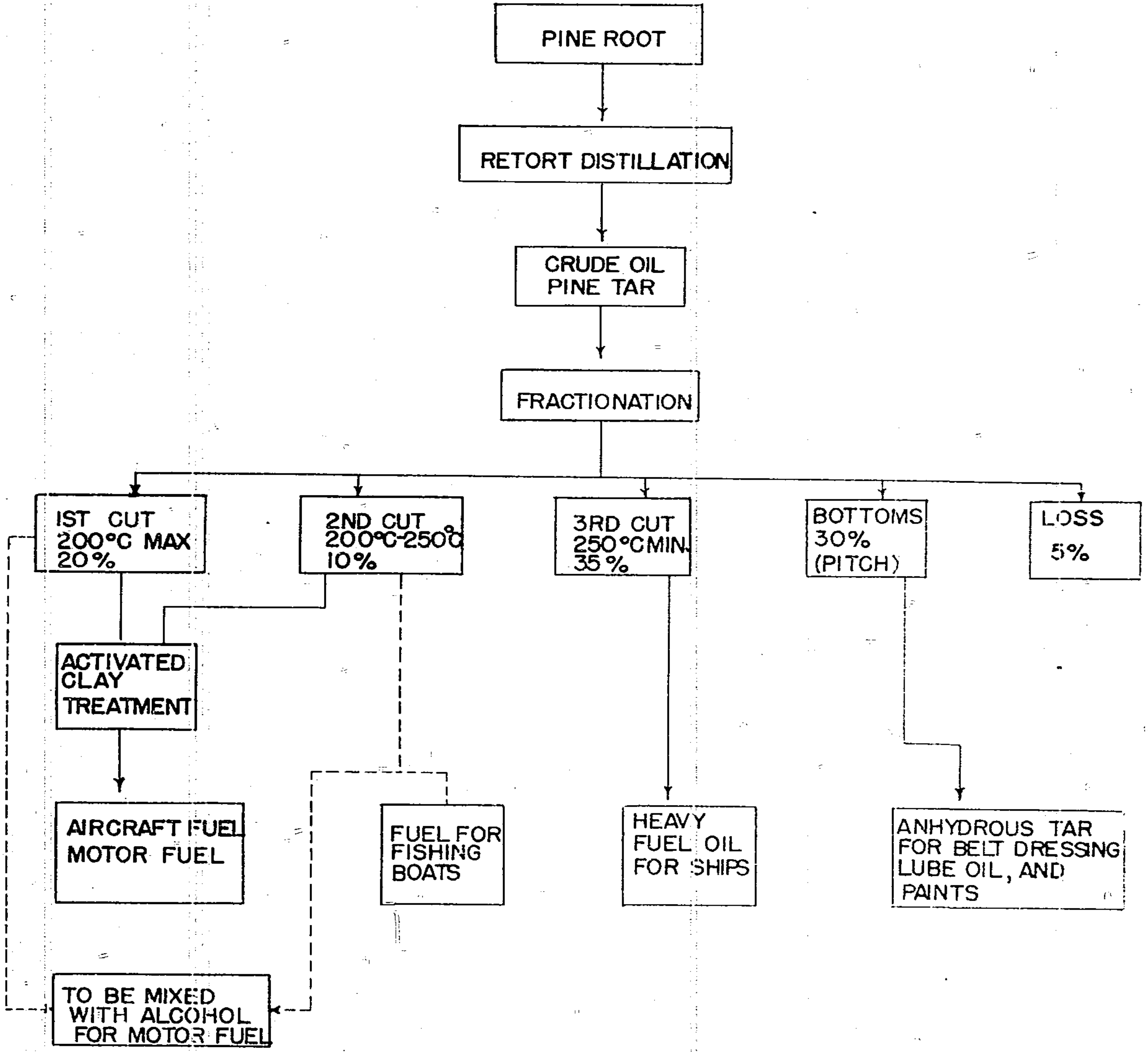
APPENDIX II

PROPOSED MATERIAL FLOW DIAGRAM

SHIMABARA RESIN-OIL FACTORY



DOTTED LINES REPRESENT ALTERNATE APPLICATIONS

ENCLOSURE (E)

ENCLOSURE (E)

LIST OF JAPANESE DOCUMENTS PERTAINING TO PINE ROOT OIL

(Forwarded through ATIS to Washington Document Center)

NavTechJap No.	ATIS No.	Title
ND26-0010	4581	"Pine Root Oils," published by First Naval Fuel Depot, OFUNA, 30 January 1945 (Translation included as Enclosure C)
ND26-0018.1-2	4589	Report of laboratory and pilot plant results in processing pine root oil for the production of aviation gasoline. (Miike Synthetic Oil Co.)
ND26-0020	4591	Preparation of aviation gasoline from Japanese pine root oil. (Imperial Fuel Institute).

RESTRICTED

ENCLOSURE (F)

ENCLOSURE (F)

EXPERIMENTS ON COMBUSTION OF PINE OIL IN TURBINE ROCKETS

by

YOZO NOGAMI

ENCLOSURE (F)

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LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (F)

(These experiments were carried out at the Institution of Technical Reserve of the Japanese Navy from June 10th, 1945 to August 15th, 1945.)

A. Description of Apparatus Used in Experiments

1. Axial flow fan--20 stages. Efficiency 85% (Full load). Capacity; 2.26 kg/sec at atmospheric pressure (8,000 RPM).

2. Starting motor--50kw Shunt type.

3. Model combustion chamber--1/12 of the original size, not geometrically similar. Made of mild steel plates 1.5mm thick.

4. Fuel injection nozzle--Solid injection type and air injection type were both tested.

5. Fuel pump--IMO pump (worm gear type). Maximum delivery pressure 20 kg/cm^2 (gauge).

6. Fuel tank--Provided with level indicator to show fuel consumption.

7. Fuel preheater--5kw electric furnace.

8. Air compressor for injecting air--100hp reciprocating type.

9. Air reservoir.

1. and 2. were taken from a Velox boiler designed by Brown Bovery & Co.

Following quantities were measured:

At (a) and (b) -- Amount of air with an orifice.

(c) -- Pressure and temperature of fuel with a Bourdon gauge and a mercury thermometer.

(d) -- Pressure of injection air with a Bourdon gauge.

(e) -- Temperature of gas using a Pt-Pt·Rh thermocouple.

(f) -- Temperature and composition of gas using an Almel-Chromel thermocouple and an Orsat gas analyzer.

(g) -- Pressure, temperature and velocity of air using water-column manometer, a mercury thermometer and a Pitot tube.

(h) -- Amount of fuel by reading displacement of level indicator during a given time.

(i) -- Amount of air injected using an orifice.

Figure 2(F) shows the detail of a model combustion chamber and Figure 3(F) a rough sketch of fuel injection nozzles.

B. Experimental Conditions

1. Kind of fuel -- Pine Root Oil (heavy; crude).

2. Fuel injection nozzle -- Air injection type.
   Air pressure-2.5 -4.0 kg/cm^2 (gauge)
   Oil pressure-10 kg/cm^2 (gauge)
   Solid injection type
   Oil pressure -15 kg/cm^2 (gauge).

3. Pressure in combustion chamber -- Atmospheric.

4. Amount of combustion air -- Up to 2.26 kg/sec

5. Amount of fuel -- Up to 20 gm/sec

6. Air ratio -- Before the cone 16-20
   After the cone 90-110.

7. Maximum combustion chamber lead -- 12,000 kg of fuel/m^3 of combustion chamber/hr.

8. Temperature of gas at the outlet of the chamber -- 500°C -800°C.

9. Preheating of fuel -- Up to 90°C.

C. Summary of Results

1. Crude pine root oil burned fairly well in this type of combustion chamber. The following two short-comings were noticed:

   a. The oil contained a large amount of impurities so that the capacity of the fuel filter should be increased.

   b. As the oil was rather viscous, it was necessary to preheat it, and after cooling down, the fuel line was frequently clogged.

2. Heavy pine root oil was much more difficult to burn than crude pine root oil. Solid injection type nozzles were unsuitable, and air injection type whould be adopted, though the latter required an additional compressor.

3. The type of combustion chamber now in use gave satisfactory results. By the cooling effect of the secondary air, the chamber wall was kept at a comparatively low temperature, and the cone gave good mixture of primary and secondary air.

4. A combustion chamber load of 12,000 kg/m^3 hour was possible even with heavy pine oil (using air injection nozzle). But by using these fuels in an actual engine, many difficult problems will be encountered as mentioned above.

D. Conference on Fuel Test for Gas Turbine Rockets, at the First Naval Technical Arsenal, June 16, 1945

1. Purpose of Conference: To discuss the possibility of utilizing pine root oil for gas turbine rockets and to decide the method and research period for the experiments.

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2. Fuel Test Schedule.

Item	Place and Personnel	Appointed Date of Completion
1. Combustion tests with old type engines.	At HATANO Branch Arsenal.	
a. Heavy pine root oil. Heavy pine root oil alone. Heavy pine root oil and gasoline (90%, 80%, 70%)	Lt. Cmdr. NAGANO	June 18th
b. Crude pine root oil. Crude pine root oil alone. Crude pine root oil and gasoline (90%, 80%, 70%)	Lt. Cmdr. NAGANO	June 26th
2. Combustion tests with improved engines using heavy pine oil and gasoline.	At TOHOKU Imperial University	
a. Elementary researches with models.	Professor TANAZAWA	July 25th
b. Tests with actual engines.	At the Institution of Technical Research. Lt. NOGAMI	

3. Combustion tests on heavy pine root oil alone.

   a. Combustion tests with solid injection nozzles.

   b. Combustion tests with air injection nozzles.

Progress on Development of Combustion Chambers (cf. Figure 4(F)), in Actual Engines.

No.	Peculiarities	A_1 (cm^2)	A_2 (cm^2)	A_2/A_1	a_1 (cm^2)	a_2 (cm^2)	a_3 (cm^2)	a_4 (cm^2)
1	Unburnt fuel drops come out of chamber.	278	254	0.92	270	180	342	228
2	Form of cone altered. No unburnt fuel but back firing occurs.	275	338	1.23	263	180	449	293
3	To avoid back firing, the secondary air passage area was diminished.	275	338	1.23	263	180	270	180

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Results of Tests at the First Naval Technical Arsenal (cf. (B),1,(a).

Test No.	Fuel		Starting	Acceleration	Full load	Specific Gravity of Fuel
	Heavy Pine Root Oil.	Gasoline				
1	80%	20%	Difficult	Impossible	See Note	0.945
2	70%	30%	Easy	See Note	See Note	0.919
3	60%	40%	Easy	Possible	Fairly good	0.915
4	50%	50%	Easy	Easy	Good	0.868
5	30%	70%	Easy	Easy	Good	0.835
6	10%	90%	Easy	Easy	Good	0.765
7	100% Crude Pine Oil		Easy	See Note	Fairly good	0.947

Note: No. 2 and 7 of Acceleration is---Possible but difficult.
No. 1 and 2 of Full Load is---Required power developed, but general conditions are unsatisfactory.

Remarks.

1. Heavy pine root oil with more than 60% of gasoline can be used in actual engines.

2. 100% crude pine root oil showed unsatisfactory results in solid injection nozzles. Therefore, studies with air injection nozzles are necessary.

3. Fuel filters made of silk cloth are unsuitable for pine root oil.

4. Multiplate filters used in the tests lack in capacity.

5. Solid injection nozzles used in the test are not satisfactory.

Figure 5(F) shows the relation of:

Fuel comsumption B(lit/hr).
Pressure in combustion chamber P_3 (kg/cm^2 gauge).
Pressure before diffusor P_4 (kg/cm^2 gauge).
Temperature in combustion chamber T_3 (°C).
Temperature before diffusor T_4 (°C).

to the rotating speed of turbine in the same experiment.

4. The quality of pine root oil used in the experiment.
The analyses of crude and heavy pine root oil used in our institution are given in Table I(F).

5. The results of combustion tests with air and solid injection nozzles are shown in Table II(F) and Table III(F) respectively. The list of

ENCLOSURE (F)

notations used in Table II(F) and Table III(F) is as follows:

V--Speed of blower (RPM)
Pa--Pressure of injection air (kg/cm^2 gauge).
P_5--Pressure of fuel (kg/cm^2 gauge).
t5--Temperature of fuel. (°C)
t_a--Temperature of air. (°C)
T--Temperature of gas at the chamber outlet. (°C)
Q_5--Fuel consumption. (gm/sec)
W--Speed of air at the chamber inlet (m/sec)

Table I(F)
PROPERTIES OF PINE ROOT OIL

	Crude Pine Root Oil	Heavy Pine Root Oil
Specific Weight (15/4 °C)	0.9769	
Reaction	Acid	Acid
Water Content (%)	0.7	1.3
Flash Point (°C)	35.0	55.0
Freezing Point (°C)	Below - 20°C	Below - 20°C
Ash Content (%)	0.011	0.139
Viscosity (S) R-1 30°C	51.6	190.2
Cetane Number	22.4	

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Table II(F)
RESULTS OF COMBUSTION TEST WITH AIR INJECTION NOZZLES

Time	V	P_f	P_a	t_f	t_a	T	Q_f	W	Color of Smoke	Length of Flame (cm)
	RPM	kg/cm^2	kg/cm^2	°C	°C	°C	gm/sec	m/sec		
16.05	1500	15	2.5	28	36.4	398	6.54	119		65
16.10	1100	15	2.5	32	36.0	422	7.85	98		60
16.13	1100	15	2.0	34	36.0	448	8.76	91		66
16.17	1100	15	1.5	36	36.0	530	9.40	91		70
16.20	1100	15	1.0	38	36.0	565	9.57	91	Faintly black	70
16.27	1500	15	2.5	41	37.0	397	8.13	98	Faintly black	66
16.33	1600	15	2.0	42	37.0	410	8.81	100	Faintly black	64
	1600	14	1.5	42	37.0	492	8.47	100	Faintly black	68
	1600	14	1.0	42	37.0	515	8.91	99	Faintly black	
	700	15	3.0	45	34.0	545	9.34	70	Faintly white	80
	700	14	2.5	45	33.5	528	11.05	68		80
16.49	700	15	2.0	45	34.0	555	9.34	70		
17.00	700	15	1.5	45	34.0	572	9.81	69		
17.01	700	15	1.0	45	34.0	598	7.95	68	Faintly black	
17.02	700	15	0.5	46	34.0	730	8.17	68		
17.05	700	15	0.5	46	34.0	752	11.12	65		60

Fuel: Heavy pine root oil No preheating.

Table III(F)
RESULTS OF COMBUSTION TESTS WITH SOLID INJECTION NOZZLES

No	V	P_f	Q_f	t_f	Q_a	Q_i	T	Length of Flame cm
	RPM	kg/cm^2	gm/sec	°C	gm/sec	gm/sec	°C	
1	1100	13	14.1	38	226	162	850	75
2	1150	10	10.9	42	202	210	510	75
3	1600	10	10.9	42	234	241	840	50
4	1600	8	9.9	41	246	247	470	60
5	1600	8	10.4	41	252	229	530	58

Fuel: Heavy pine root oil. No preheating Solid injection

ENCLOSURE (F)

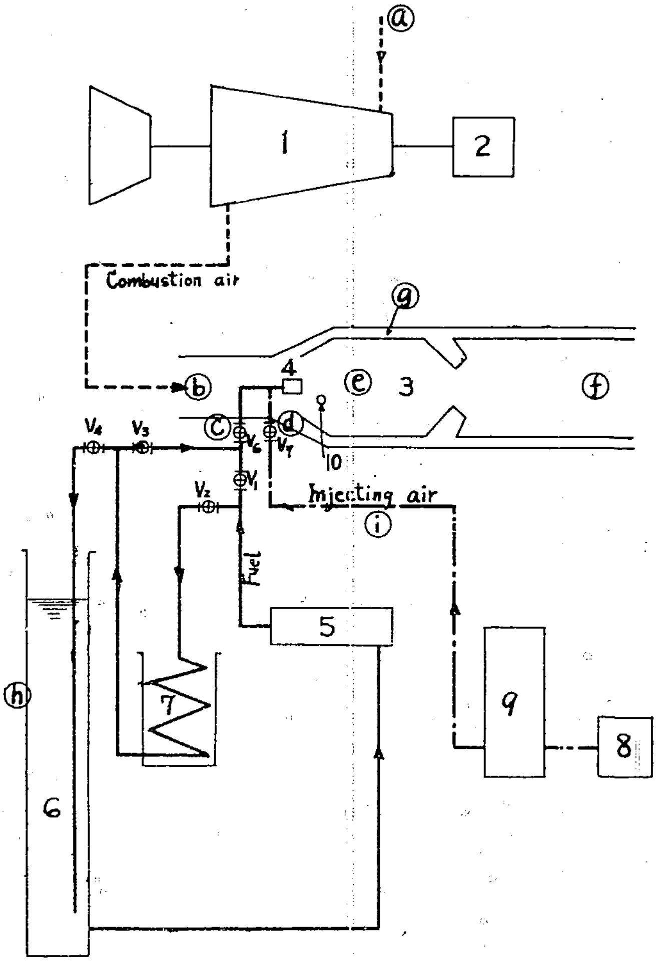


Figure 1(F)
APPARATUS OF EXPERIMENT

ENCLOSURE (F)

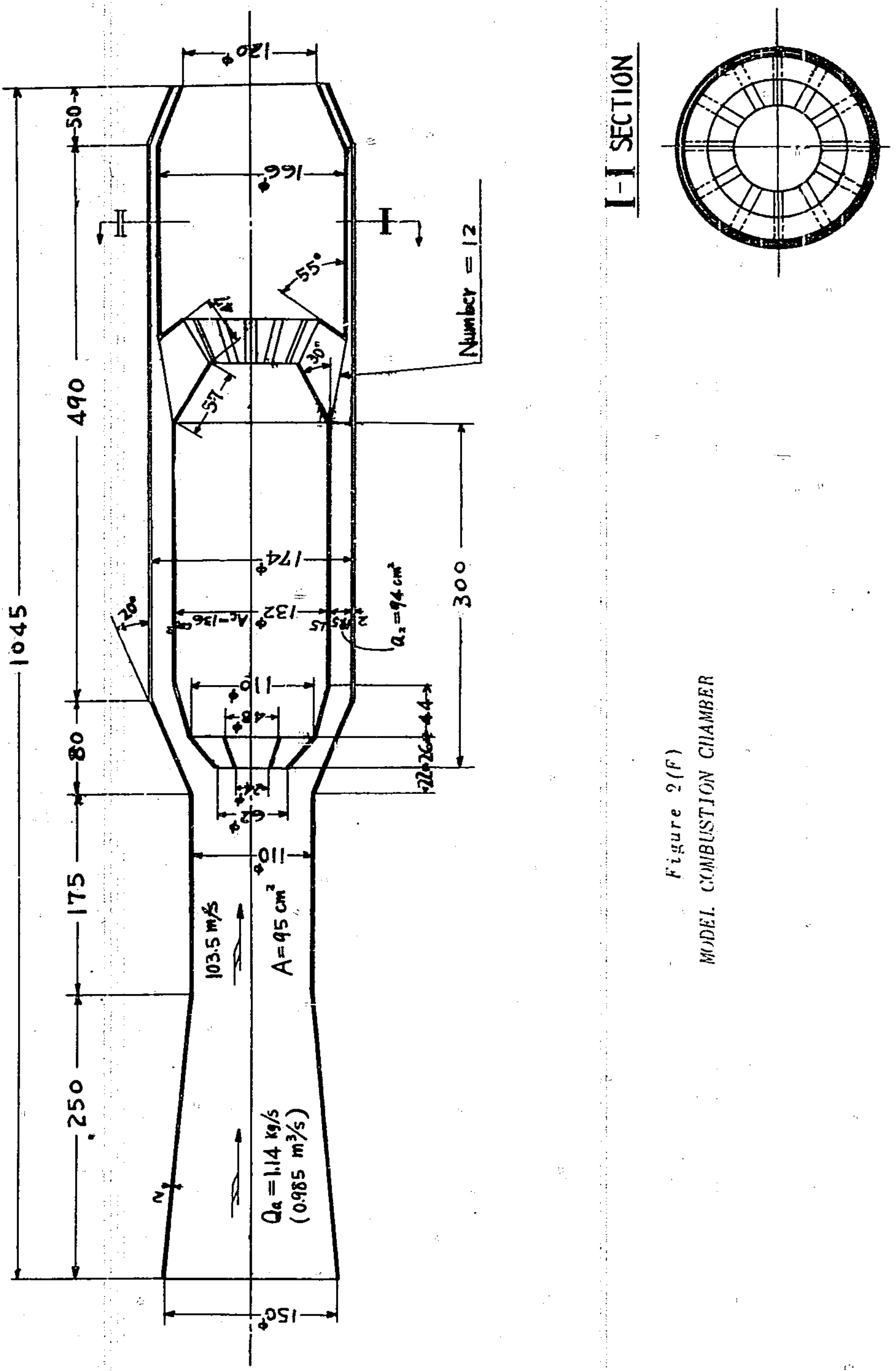
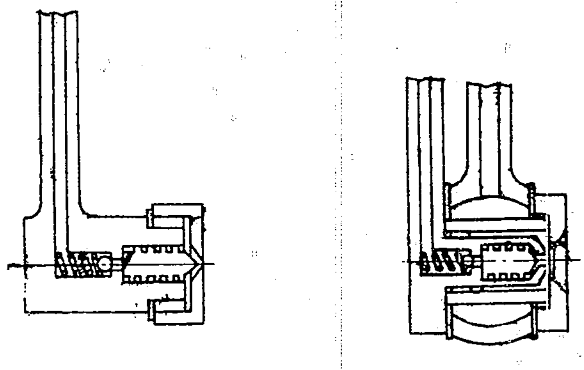


Figure 2(F)
MODEL COMBUSTION CHAMBER

ENCLOSURE (F)



SOLID INJECTION TYPE

AIR INJECTION TYPE

Figure 3 (F)
FUEL NOZZLES

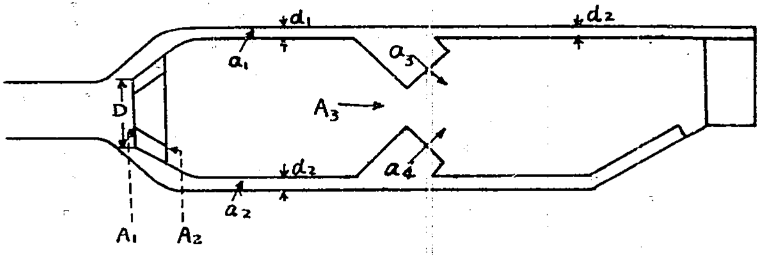


Figure 4 (F)
COMBUSTION CHAMBER

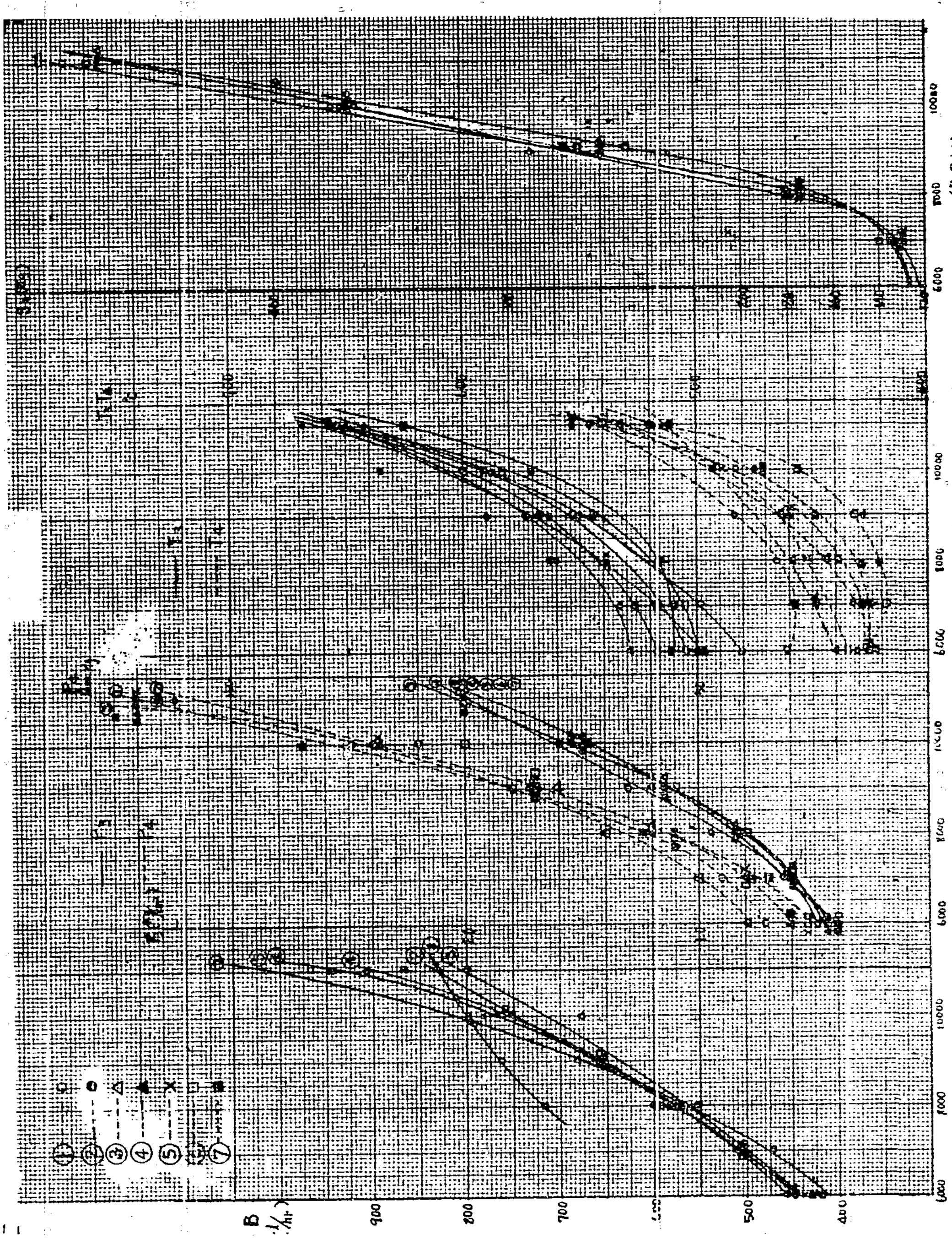


Figure 5(F)
RELATIONSHIP BETWEEN ENGINE SPEED AND INTERNAL CONDITIONS