

RESTRICTED

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

Figure 1(A) Yield of Fractions Page 19
Figure 2(A) Overall Scheme for Production of Aviation Gasoline
from Pine Root Oil Page 20

PART II

Table I(A) Compositions of Pine Root Tar and Pine Root Crude
Oil Page 36
Table II(A) Reaction Products, Dry-Distillation of Cellulose
and Lignin Page 36
Table III(A) Comparative Results, Catalytic Cracking and Reforming... Page 36

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 rosin 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.

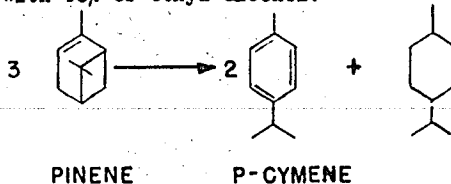
Simultaneously with these experiments, designs of commercial plants were widely investigated from the standpoint of utilizing civilian techniques and avoiding large scale plants that would require long construction periods. Chem. Eng. Lieut. Comdr. R. YUMEN constructed several types of model retorts 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.



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°C15.0%
120 to 150°C 3.0%
150 to 220°C13.0%
Residue69.0%

ENCLOSURE (A)

Pine Root Crude Oil:

Sp. Gr. (20/15°C)	0.974
n _D (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%

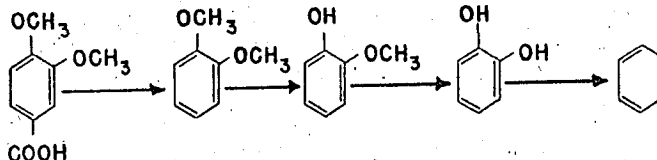
The above two oils were treated together as total pine root oil, because pine root tar solidifies in winter and is unsatisfactory for transportation.

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:

<u>Temperature °C</u>	<u>Yield (Vol%)</u>	<u>Remarks</u>
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 β -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 C₃, C₄ and C₅ etc., in the lower boiling fractions. Corrosion by fractions boiling above 250°C was negligible.

T. HIRAZUMI of the Takasego 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

ENCLOSURE (A)

residual oil. The residue, a viscous oil solidifying 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 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	-18°C
Flash point	77°C
Viscosity (R-2, 20°C)	160 sec.
Conradson's carbon	0.67%
Ash	0.08%
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)

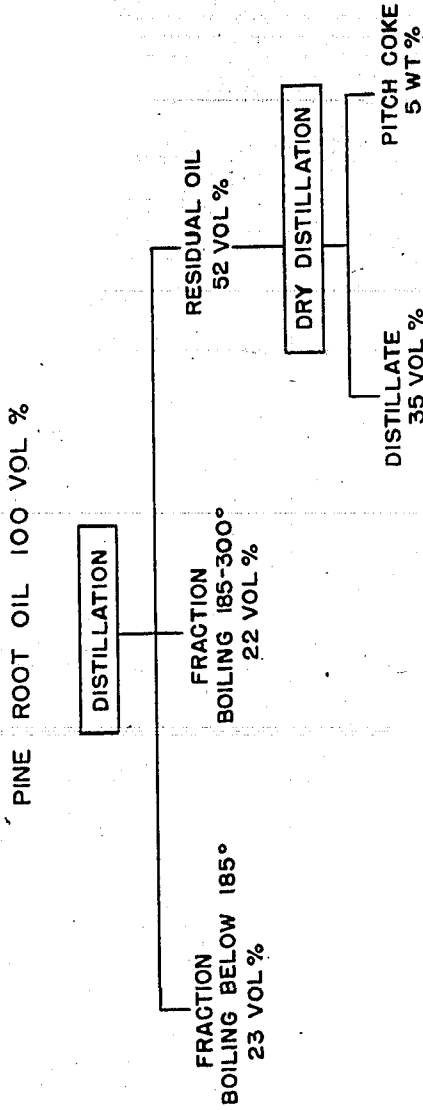


Figure 1(A)
YIELD OF FRACTIONS

ENCLOSURE (A)

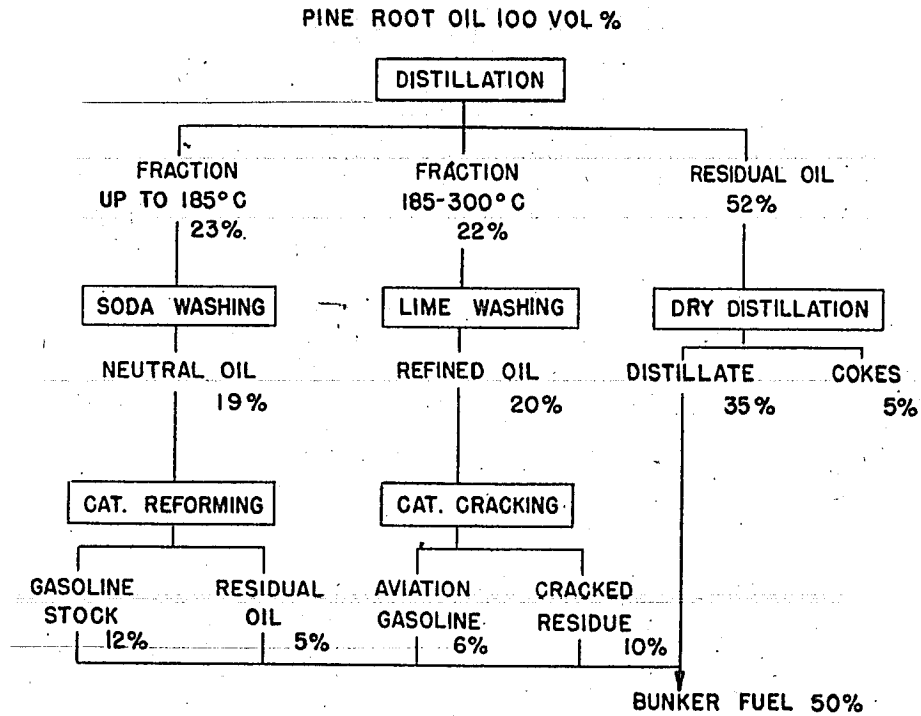


Figure 2(A)
OVERALL SCHEME FOR PRODUCTION
OF AVIATION GASOLINE FROM PINE ROOT OIL

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°C 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 terpen 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), 105). 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 MoO₃ 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.

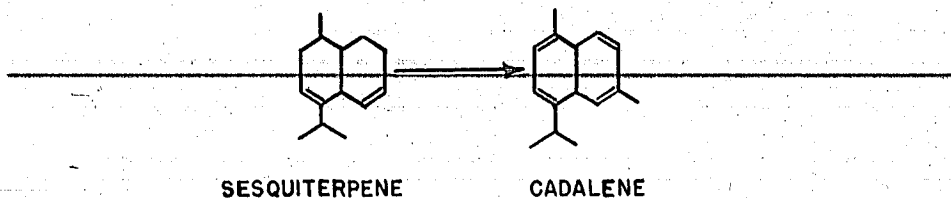
When the last fraction was distilled with acid clay at 400°C, the distillate contained 60% retene.

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 HIRAZUMI, 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 guaiacool 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 Todometsu 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)

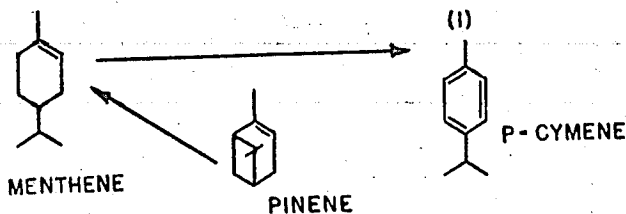
Furthermore, Ruzicka and his co-workers (Hel. 5, (1922), 345) succeeded in determining the structural formula of sesquiterpenes, using the Vesterberg process by converting the terpenes into cadalene or eudalene.

ENCLOSURE (A)



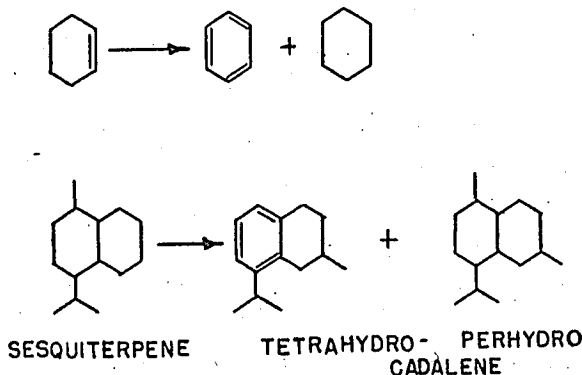
In 1903, Vesterberg (Ber. 36 (1903), 4200) reacted pure abietic acid $C_{19}H_{29}CO_2H$ with sulphur, and obtained retene $C_{19}H_{18}$ as the chief product.

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.



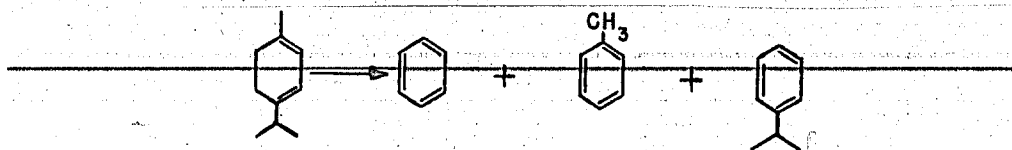
One thing to be noticed in connection with the preceding paragraph, is the catalytic transformation of terpenes, investigated by S. KIMURA (Mem. Coll. Sc. Kyoto I.U.A. 14 (1931), 173). This reaction occurs in the catalytic reformation of pine root oil.

Catalytic auto-oxidation and reduction reactions of these compounds are well known or have been reported. Δ^1 -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).

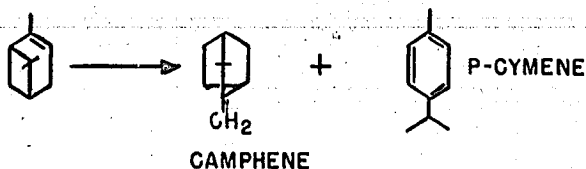


p-Cymene has been decomposed into benzene, toluene and cumene, by the catalytic action of acid clay at 350-400°C, according to T. OKADA (unpublished).

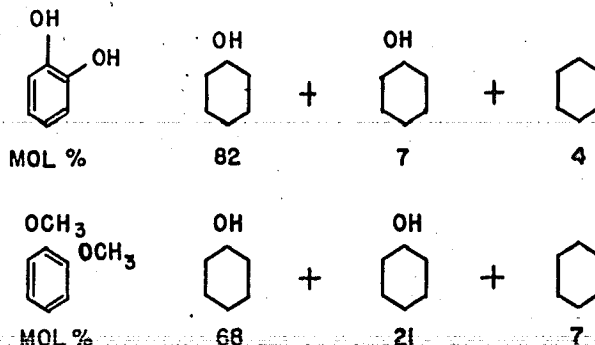
ENCLOSURE (A)



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)



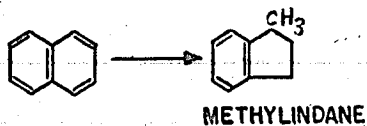
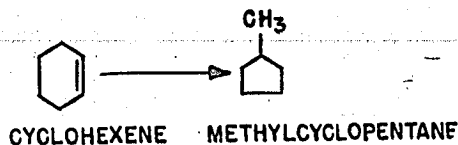
Toluene, benzene and phenol have been formed by thermal decomposition of cresols (R. NAKAI, Bull. Chem. Soc. Japan 5 (1930), 136), as a result of demethylation. The case of demethylation from benzene nuclei is in the order para, ortho, meta. The methyl or hydroxyl group in phenol derivatives, situated 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 pentamethylene derivatives are formed as follows:



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