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ENCLOSURE (B)2

STUDIES ON THE CARBONIZATION OF RESIN

by

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Research Period: 1944-1945

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

December 1945

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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. INTRODUCTIONA. History of Project

The essential components of crude pine resin are mono-, sesqui-, and di-terpenes 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
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II. DETAILED DESCRIPTIONA. Test Apparatus

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

T ₁ = Thermometer	H = Heater
T ₂ = Thermocouple	C ₁ , C ₂ = Condenser
F = Distillation Flask	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

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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 MoO₃ and 3 parts of acid clay) were placed in the apparatus. After purging the air with hydrogen gas, the pressure of H₂ was raised to 100 kg/cm². About 7 hours were required to heat up to 450°C, 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-distillationa. 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 CO₂ occurred at 300°C as was the case in the dry distillation. The effect of wood charcoal on the carbonization was not

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appreciable but it did decrease the decomposition temperature and, by adsorption, tended to slow down the distillation of the 185^o-300^oC 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^oC and is thought to be mainly the decomposition of the C-COOH bond. The 2nd reaction taking place at approximately 320^oC was that of de-isopropylation since the gases obtained at that temperature were composed 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^oC 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(E)2.

Sample treated.about 1.01
Reaction Temperature.400^oC
Catalyst.acid clay
Space Velocity.1.0

4. Catalytic Hydro-cracking

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

Reaction Temperature..... 450^oC
Sample treated..... 300cc
Catalyst..... No. 105
Reaction time..... 1 hour
Apparatus..... Rolling type Autoclave
Initial Pressure kg/cm²..... 100
Reaction Pressure kg/cm²..... 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^oC

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

Sp. Gr. 25/4. 0.9740
Flash point ^oC 131
Freezing point ^oC below -15^oC
Viscosity at 0^oC sec
Redwood No. 1 327.6

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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

- 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.
- Wood charcoal does not serve to lower the acid value of the 185 to 300°C fraction.
- Acid clay serves the following purposes:
 - The deoxygenation & dehydration reaction occurs at 200°C.
 - 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.
- By catalytic reforming, high octane value gasoline is obtained but the distillation curve is not suitable for aviation fuel, therefore the gasoline can be used only for blending.
- By catalytic hydro-cracking a high quality aviation gasoline is obtained.
- 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

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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 _m H _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 ²⁰	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 ²⁰	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

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Table IV(B)2
YIELD OF 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, l	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 _m H _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_D^{15}	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_D^{15}	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_D^{15}	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

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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							
	300	250	300	340	380	420	450	200	220	250	300	320	340	380	420	
Temp. (°C)	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	
CO 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 ₂ H ₄ (%)	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	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	

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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 _D ¹⁵	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 _D ¹⁵	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 _D ¹⁵	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 _D ²⁰		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

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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
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

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T₁ = THERMOMETER
T₂ = THERMO-COUPLE
F = DISTILLATION FLASK
R = RECIEVER FOR DISTILLATE
H = HEATER
C₁, C₂ = CONDENSER
G = GAS METER

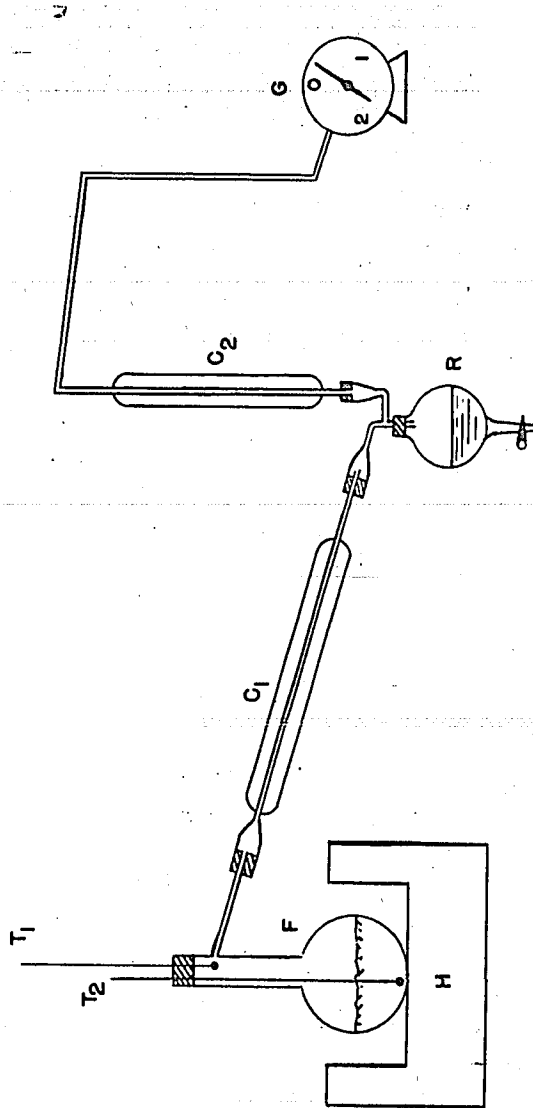


Figure 1(B)2
APPARATUS FOR THE CARBONIZATION OF PINE RESIN