ENCLOSURE (B) 15

STUDIES ON THE PROPERTIES OF TAR FROM COAL HYDROGENATION

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

The tar from the South Manchurian Railway Co. coal hydrogenation works at FUSHUN was investigated to determine the properties and composition of its light oil (boiling up to 220°C) and heavy oil (boiling 220-280°C).

The crude tar contained 20-30% of phenolic substances which were mostly in the fractions boiling from 165 to 245°C. The chemical constituents in the neutral oils from the light and heavy oils were as shown in Table I(B)15

Aviation gasolines were prepared by two methods from the neutral light oil; (1) by distillation and (2) by hydrogenation and distillation.

The properties of these two aviation gasolines were as shown in Table II(B)15.

The gasoline made by hydrogenation of the neutral oil was far superior to that obtained by straight distillation.

A number of pure hydrocarbons were identified in the crude tar, acidic fractions of the crude tar, and aviation gasoline from hydrogenated oil.

I. INTRODUCTION

The present investigation was made to determine (1) the quality of gasoline obtained by hydrogenation of coal, and (2) to obtain data on hydrocarbon composition which might be useful in improving the process.

The work was started in 1939 and completed in 1940. The key research personnel were Comdr. T. YOKOTA and Nav. Eng. K. MITSUI.

II. DETAILED DESCRIPTION

A. Crude Tar and Neutral Oil.

The crude hydrogenated tar was obtained from the South Manchurian Railway Co. plant at FUSHUN. At this plant, OYAMA coal was hydrogenated over an Fe_2O_3 catalyst at 410°C and 200 atmospheres. This tar had a deep brownish color, which gradually became darker on standing in air. Some solid matter was held in suspension. The crude tar and neutral oil obtained by dephenolating the crude tar with 10% caustic soda solution, were distilled and the results are given in Table III(B)15.

It can be seen from the table that the acidic oil is contained in the fractions boiling above 200°C.

B. Light and Heavy Oils From Crude Tar.

Light and heavy oil fractions, obtained by fractionation of the crude tar were analyzed for hydrocarbon composition by the usual methods, and the results are given in Table IV(B)15.

C. Neutral Oil From Crude Tar

Neutral oil from crude tar was dried with anhydrous sodium sulphate, distilled carefully, and the composition and property of each fraction

determined. The results are given in Table V(B)15.

The lighter neutral oil fractions were rich in naphthenic compounds, whereas the heavier fractions were rich in aromatics.

Next, these fractions were studied to determine naphthenic and aromatic compounds present, and various compounds were isolated. The amount of these compounds present was not determined. The results are shown below.

Fraction	Compounds Isolated In Neutral Oil.
1	Benzene, Methyl-cyclopenthane.
2	Toluene, Cyclohexane, Methyl-cyclohexane.
3	o,m,p--Xylenes.
4	Mesitylene
5	Tetralin, Di-hydro-naphthalene.
6	Naphthalene, Hydro-naphthalene (?)
7	a,b--Methylnaphthalenes.
8	a,b--Methylnaphthalenes.
9	b,b'-Dimethylnaphthalene.
10	b,b'-Dimethylnaphthalene.

D. Acidic components in crude tar

Crude tar was fractionated into 21 cuts, and the phenolic content of each fraction was determined by treatment with 10% NaOH. The results are shown in Table VI(B)15.

The acidic components were mostly contained are in the fractions boiling from 165-245°C.

To confirm this, the caustic-soluble fraction obtained in the preparation of neutral oil was treated with 10% HCl to produce free acidic oil. The acidic oil was fractionated as follows:

Fraction	Vol. %
i.p. -215°C	21
215-225	33
225-235	19
235-245	12
245-255	8
255-265	4
265-275	4

The above fractions were each redistilled and the resulting cuts recombined to give close boiling range fractions. From ultimate analyses and molecular weight determinations, the components were identified as shown below.

Fraction	Constituent
195-200°C 200-205	o,m,p,-Cresols: C_7H_9O
206-215 214-221 221-228	Xylenols: $C_8H_{11}O$
230-240	Phenols: $C_9H_{12}O$
240-245 245-248	Phenols: $C_{10}H_{13}O$

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E. Aviation Gasoline

1. An aviation gasoline was prepared from neutral light oil by distillation and final treatment with 10% caustic soda solution. The properties of the gasoline are given in Figure 1(B)15 and listed below.

Unsaturates	5.3
Aromatics	24.2
Naphthenes	39.3
Paraffins	31.2
Sulphur (wt %)	0.15
Octane no.	69
Clear with 0.1% lead	82

2. An aviation gasoline was also prepared from neutral gas oil (boiling range of 200-230°, d_{15}^{15} = 0.879), which was hydrogenated over Ni_2O_3, MoO_3 clay catalyst (wt. ratio of 1:2:3), at 450°C under 270 atm. pressure of hydrogen and S. V. of about 2. The yield of hydrogenated oil was 88% by weight.

The hydrogenated oil (44-263°C) was fractionated and the results compared with the original gas oil sample (Table VII(B)15.

Aviation gasoline with properties shown below was prepared with a yield of 26% by fractionation of the hydrogenated oil.

Density (20/4 °C)	0.7348
Solid Point (°C)	-50
Vapor Press (kg/cm^2)	0.427
Gummy Matter (mg/100cc)	4.6
Sulphuric Acid Absorption (%)	0.5
Content of C. (wt %)	86.04
Content of H. (wt %)	13.87
Content of S (wt %)	0.01
Engler Distillation (Vol. %)	
I.B.P.b	51.0°C
10%	64.5°C
20%	71.0°C

The hydrogenated aviation gasoline was fractionated into 8 cuts, and the octane number of each cut determined (Table VIII(B)15).

The hydrogenated aviation gasoline was closely fractionated in a podbialniak still, and the following compounds were isolated from each cut.

Fraction (°C)	Compound
I.P. - 30	n-Butane, iso-Pentane, n-Pentane.
45 - 50	n-Pentane, Cycloptane, Neohexane, 2-Methyl-pentane.
70 - 75	n-Hexane, Methyl-cyclo-pentane, Benzene, Cyclo-hexane.
75 - 81	2,2-Dimethyl-pentane, Benzene, Cyclohexane. 2,4-Dimethyl-pentane, 3,3-Dimethyl-pentane.
98 - 101	n-Heptane.
101 - 111	Toluene

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III. CONCLUSIONS

Tar prepared by the hydrogenation of coal, was obtained in yield of 77 % on ash-free coal. It consisted of 26% acidic, 4% basic and unsaturated, and 67% neutral substances. The neutral part of the tar was composed of 31% paraffins, 15% naphthenes and 54% aromatic compounds. The acidic compounds were mostly contained in the crude light oil fraction.

The crude heavy oil, used for making paste with coal, which boiled from 220 to 280°C, was composed of 28% paraffins and 36% aromatics.

The aviation gasoline derived from the hydrogenated neutral light oil, showed an octane value of 90 with 0.1% lead.

Table I(B)15
COMPOSITION OF OILS

	Aromatics	Naphthenes	Paraffins
Light Neutral Oil	43	4	49
Heavy Neutral Oil	60		36

Table II(B)15
COMPOSITION AND OCTANE NUMBER OF THE GASOLINES

	Component			Octane Value	
	Aromatics	Naphthenes	Paraffins	Clear	0.1% Lead
Neutral Oil Distillation	24	39	31	69	82
Hydrogenated Neutral Oil	14	38	48	73.8	90.5

Table III(B)15
DISTILLATION OF CRUDE TAR AND NEUTRAL OIL

Engler Distillation	Crude Tar (A)	Neutral Oil (B)	A -
~ 105°C		0.1 Vol.%	
105 ~ 115	0.4 Vol.%	0.2	0.2
115 ~ 125	0.6	0.2	0.4
125 ~ 135	0.7	0.5	0.2
135 ~ 145	0.8	0.7	0.1
145 ~ 155	1.1	1.0	0.1
155 ~ 165	1.4	1.5	-0.1
165 ~ 175	2.3	2.0	0.3
175 ~ 185	3.5	2.7	0.8
185 ~ 195	5.0	3.5	1.5
195 ~ 205	7.6	4.9	2.7
205 ~ 215	11.0	7.3	3.7
215 ~ 225	14.0	8.4	5.4
225 ~ 235	16.2	11.7	3.5
235 ~ 245	19.5	13.8	5.7
245 ~ 255	22.8	17.5	5.3
255 ~ 265	27.8	22.3	5.5
265 ~ 275	32.3	24.5	7.8
275 ~ 285	37.2	28.5	8.3
285 ~ 295		32.0	
295 ~ 300		35.0	

Table IV(B)15
PROPERTIES OF CRUDE TAR FRACTIONS

	Light Oil	Heavy Oil
Boiling Range (°C)	below 220°C	220-280°C
Specific Gravity d_{15}^{15}	0.875	0.949
Acidic Substances (Vol.%)	26.0	27.0
Yield from Tar (Vol.%)	14	23
Base unsat. (Vol.%)	7.5	10.3
Paraffins (Vol.%)	28.3	18.2
Naphthenes (Vol. %)	8.9	8.4
Aromatics (Vol. %)	29.3	36.1
Water (Vol. %)		0.3
Flashpoint (°C)		115
Viscosity (Red. 1) 40°C		12.6
Conradson's Carbon (wt. %)		0.73
Net Heat of Combustion (Cal/gr.)		10.269

Table V(B)15
PROPERTIES OF NEUTRAL OIL

Fraction	d_4^{20}	n_D^{25}	Composition			
			Unsats.	Arometics.	Naph.	Paraff.
75 - 85°C	0.745	1.414	15	8	55	22
95 - 105	759	425	14	15	45	26
115 - 125	781	432	13	25	29	29
135 - 145	808	454	8	35	18	38
155 - 165	815	461	6	43	10	40
175 - 185	840	474	4	48	7	41
195 - 205	865	490	4	53	1	42
215 - 225	876	495	3	56		40
235 - 245	896	510	3	59		48
255 - 265	918	523	5	60		35
275 - 285	927	528	4	60		34

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Table VI(B)15
PHENOLIC CONTENT OF CRUDE TAR FRACTIONS

Fraction	Yield (Vol.%)	Phenolic Content (Vol. %)
-75°C	2.3	
75-85	0.6	
85-95	0.8	
95-105	1.5	0.2
105-115	1.7	0.2
115-125	1.5	0.3
125-135	1.7	0.4
135-145	2.4	0.9
145-155	2.4	2.3
155-165	2.9	3.9
165-175	3.3	6.0
175-185	2.6	5.8
185-195	3.3	8.0
195-205	6.1	15.7
205-215	8.7	19.3
215-225	8.3	13.2
225-235	8.7	9.2
235-245	9.8	6.0
245-255	10.0	3.8
255-265	9.9	2.7
265-275	11.5	1.9

Table VII(B)15
COMPARISON OF CHARGE AND HYDROGENATED PRODUCT

Boiling Point (°C)	Neutral Gas Oil (Vol.%)	Hydrogenated Oil (%)
60		0.7
70		1.4
80		3.0
90		3.0
100		4.6
110		6.5
120		9.0
130		11.0
140		13.0
150		15.0
160		18.0
170		21.5
180		26.0
190	0.4	32.0
200	5.2	40.0
210	41.0	71.0
220	78.5	86.0
230	91.5	93.0
240	96.0	95.5
250	98.5	96.5
260		97.0

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Table VIII(B)15
OCTANE NUMBER OF HYDROGENATED AVIATION GASOLINE CUTS.

Fraction (°C)	Octane Number	
	Clear	With 0.1% Lead
I.P.- 60	78.2	101.3
60- 70	72.4	92.1
70- 80	73.9	91.4
80- 90	73.1	89.6
90-100	69.2	86.3
100-110	72.1	87.7
110-120	68.8	85.4
120-130	63.5	81.5
30%	77.5	
40%	83.0	
50%	89.0	
60%	95.5	
70%	103.5	
80%	114.5	
90%	135.0	
Dry pt.	177.5	
Components (Vol.%)		
Unsaturates	1.0	
Aromatics	13.8	
Naphthenes	37.8	
Paraffines	47.7	
Octane Number	Clear	74
	0.1% Leaded	91

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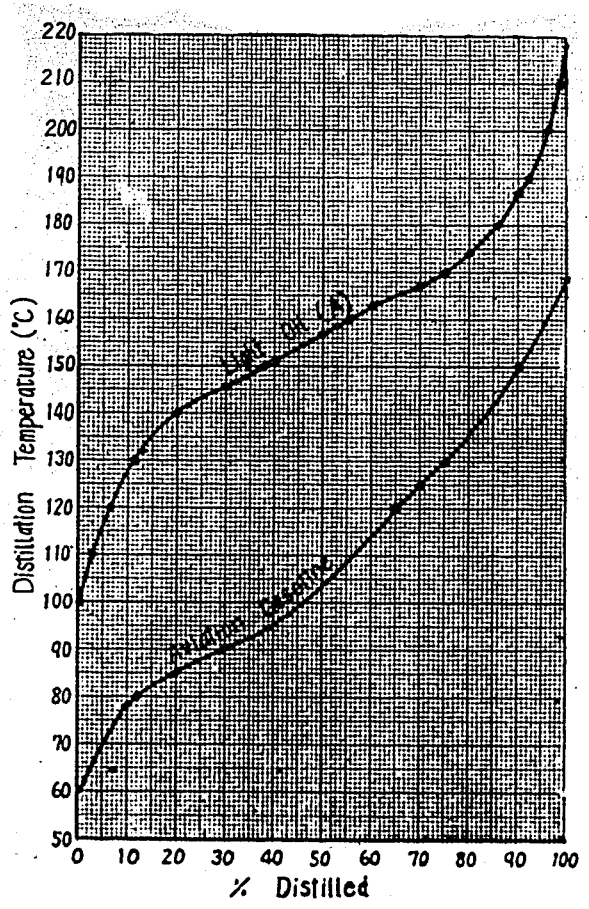

Figure 1(B)25

DISTILLATION CURVE OF GASOLINE