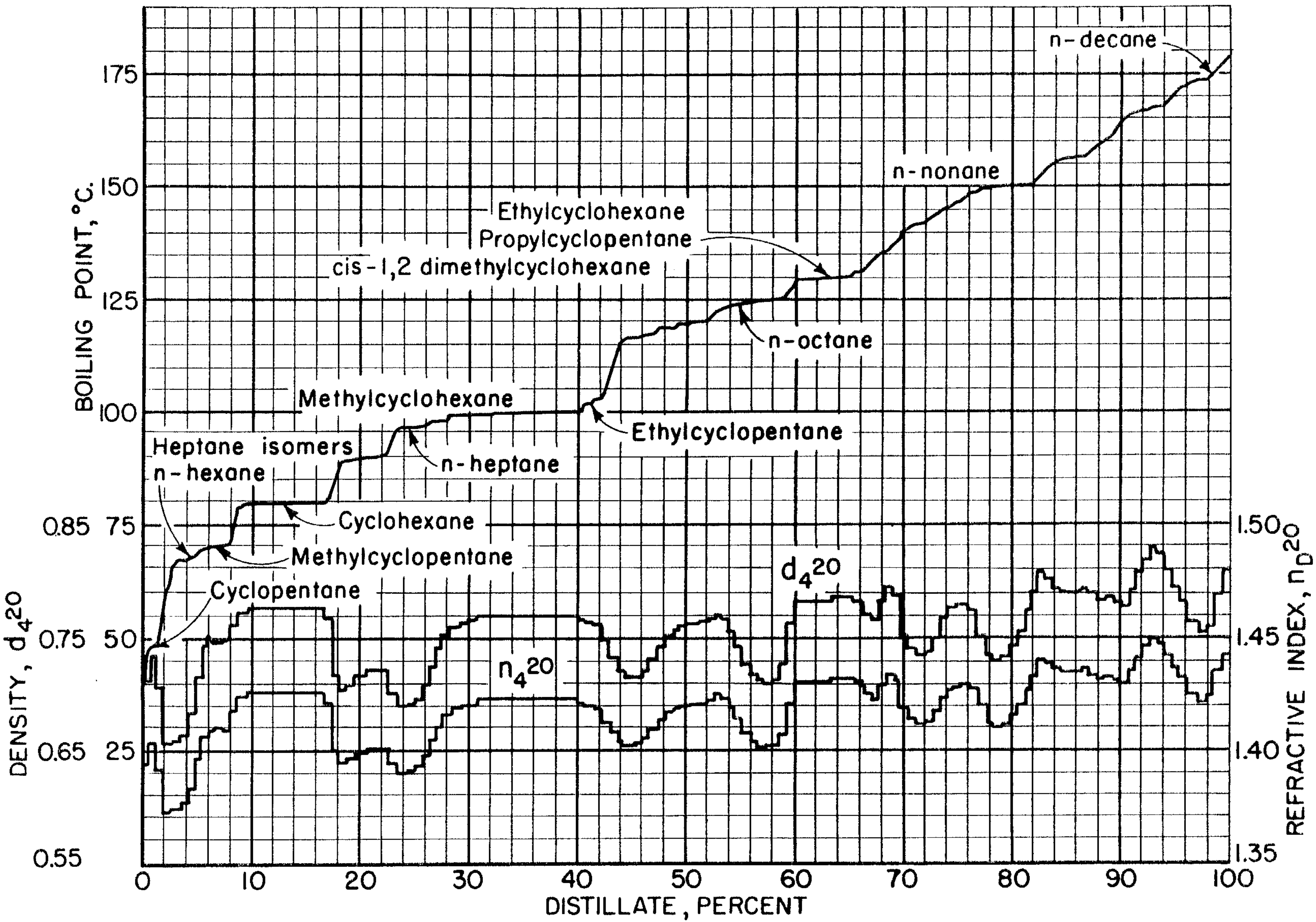

Figure 5.— Precise distillation of paraffin-naphthene fraction of neutral oil (-175°C.) from low-pressure hydrogenation of Bruceton coal.

TABLE 26. - Results of infrared analysis of several low-boiling paraffin-naphthene fractions

Fraction No.	Boiling range, °C.	Composition	
		Constituent	Percent by volume of fraction
1	38-48	Cyclopentane	68
		n-Pentane	17
		2,2-Dimethylbutane	15
2	48	Cyclopentane	80
		2,2-Dimethylbutane	20
11	71	Methylcyclopentane	100
13	72-79	Cyclohexane	60
		Methylcyclopentane	40
14	79.5	Cyclohexane	95
		Methylcyclopentane	5
21	80-83	Cyclohexane	89
		2-Methylhexane	9
		2,3-Dimethylpentane	2
22	83-89	2-Methylhexane	47
		2,3-Dimethylpentane	31
		Cyclohexane	22

The percentage of paraffins and napthenes in each fraction was calculated by three different methods. From the values thus obtained, the approximate composition of the nonaromatic fraction (table 27) of the neutral oil was estimated. Naphthenes comprised 74 percent and paraffins 26 percent of the total nonaromatic fraction.

All the normal paraffin hydrocarbons, from pentane through decane, were probably present, as well as some isoparaffins. The naphthenes, cyclopentane and cyclohexane, and their non-alkyl and poly-alkyl derivatives also were present in considerable quantities. The single compound present in greatest quantity was methylcyclohexane; it comprised 12.5 percent of the total paraffin-naphthene fraction investigated.

Heavy Oil.

The main product of the low-pressure hydrogenation of coal was "heavy oil", boiling above 250°C. It represented about 54 percent of the moisture- and ash-free coal.

TABLE 27. - Approximate composition of the paraffin-naphthene fraction of the neutral oil (87.5 percent of neutral oil), percent by volume

Compounds	Percent of paraffin-naphthene fraction	Percent of light oil
Cyclopentane	0.9	0.1
n-Hexane	2.0	.3
Methylcyclopentane	3.0	.5
Cyclohexane	8.2	1.3
Isomeric heptanes	2.0	.3
Dimethylcyclopentanes	1.9	.3
n-Heptane	3.0	.5
Methylcyclohexane	12.5	2.0
Ethylcyclopentane	2.0	.3
Isomeric octanes	3.4	.5
Dimethylcyclohexanes	4.7	.8
n-Octane	3.8	.6
Isopropylcyclopentane	.9	.1
Ethylcyclohexane Propylcyclopentane	5.1	.8
n-Nonane Isomeric decanes	3.0	.5
Methyl-ethylcyclohexanes	2.5	.4
Propyl and Isopropylcyclohexane	3.8	
Methyl-,propyl-, and methyl-isopropylcyclohexanes	3.0	.5
n-Decane	.9	.1
Diethylcyclohexanes	.5	.1
Other naphthenes in distillate	15.4	2.5
Other paraffins in distillate	7.6	1.2
Residue, b.p. $>179^{\circ}$C	9.4	1.5
Total naphthenes, b.p. $<179^{\circ}$C	64.7	10.4
Total paraffins, b.p. $<179^{\circ}$C	25.7	4.1

Distillation according to the method of the American Wood Preservers Association[96] showed the following product distribution: 0.5 percent boiled from 100° to 210°C.; 2 to 3 percent, 210° to 235°C.; 9 percent, 235° to 270°C.; 15 percent, 270° to 315°C.; and 20 percent, 315° to 355° C.[97] Thus, a total of about 47 percent of the heavy oil distilled below 355°C. at atmospheric pressure by this standard analytical test procedure.

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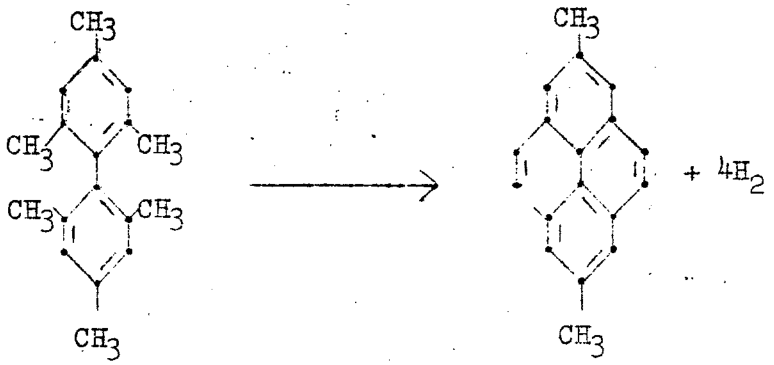
[96] American Society for Testing Materials, Standard Method of Test for Distillation of Creosote: Standards, 1942, part II, p. 679.

[97] Kaplan, E. H., Storch, H. H., and Orchin, M., Work cited in footnote 84.

When the heavy oil was distilled at 10 mm. pressure, 51 percent of the material was collected as distillate (285°C. end-point).[98] The distillate was extracted with acid and alkali; 74 percent of the material remained as a neutral portion. The neutral portion was chromatographed on alumina and separated into three fractions. The least strongly adsorbed fraction (80 percent of the neutral portion) was redistilled; the higher-boiling of the two distillate fractions (63 percent of the neutral portion) was rechromatographed and separated into four bands on the basis of increasing strength of adsorption. The least strongly adsorbed band (I) was fractionally distilled in vacuo, and small volumes of distillate were collected separately. Ultraviolet spectra were determined on each of the fractions. They all gave similar spectra; these indicated that this material (about 10 percent of the neutral oil) consisted of tetralin and naphthalene derivatives with various numbers and kinds of alkyl side chains. Bands II and IV were not investigated. The material on band III (about 18 percent of the neutral oil) was distilled in vacuo into 28 fractions. The fractions collected toward the end of the distillation were all solid at room temperature. Repeated recrystallization of these fractions gave the following pure compounds: Anthracene, phenanthrene, pyrene, and chrysene. These were all identified by melting-point and mixed melting-point determinations with authentic specimens. Phenanthrene and pyrene were obtained in about 3 percent yield from band III; the other compounds were isolated only in very small quantities. The investigation was not directed at isolating these particular compounds; the other fractions, not investigated, probably contained greater quantities of polynuclear aromatic hydrocarbons.

A small quantity of a colorless, crystalline compound, melting point 234° to 235°C., was also isolated from band III and was identified as 4,9-dimethylpyrene. Almost 3 years later this same compound was isolated in the work on a totally different project. In cyclodehydrogenation studies carried out in the investigation of the mechanism of the hydrogenation of coal, dimesityl was subjected to vapor-phase treatment over a chromia-on-alumina catalyst. A compound identical with the 4,9-dimethylpyrene obtained from heavy oil was isolated and identified by comparison of ultraviolet absorption spectra and a mixed melting point determination of the trinitrofluorenone complexes. The conversion of dimesityl to 4,9-dimethylpyrene can be written as follows:



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[98] Woolfolk, E. O., Orchin, M., and Storch, H. H., Notes on the Constitution of Heavy Oil from the Hydrogenation of Bituminous Coal: Fuel in Science and Practice, vol. 26, 1947, pp. 78-79.

Products from Hexane-Soluble Fraction of H.O.L.D. (Heavy-Oil-Let-Down) from High-Pressure Hydrogenation

The hexane-soluble fraction of total oil product (light plus heavy oil) from another high-pressure hydrogenation experiment on Bruceton coal was studied.[99] The material hydrogenated was a mixture containing 40 percent powdered coal, 60 percent heavy recycle oil (centrifuged product oil from previous runs), and MoO_3 catalyst (equal to 1 percent of the coal used). This mixture was pumped with hydrogen at 235 atmospheres through a preheater and then through two converters in series at a rate of 10.3 pounds per hour and a reaction temperature of 440°C. The contact time was 1.2 hours. The hydrogen absorption was 9.8 percent of the weight of moisture- and ash-free coal used. The average plant material balance during the period when sample was collected was 99 percent.

The particular sample of oil investigated was obtained during 32.5 hours of steady-state operation of the plant. The heavy oil product, representing about 86.5 percent of the moisture- and ash-free coal and containing the ash of the coal, the unreacted coal, insoluble organic material, and the catalyst particles, was discharged from the second converter. The heavy oil remaining after the removal of solids by centrifuging had the properties shown in table 28. The heavy oil was extracted with n-hexane; the yield of oil soluble in n-hexane was 55 percent by weight of the heavy-oil-let-down, or 48 percent by weight of the moisture- and ash-free coal. Further separation was made into acidic, basic, and neutral fractions, as shown in figure 6. The tar-base and neutral oil fractions were not investigated.

TABLE 28. - Data on heavy oil from hydrogenation of Bruceton coal

Distillation[1]		Ultimate analysis		Viscosity at 180° C.
	Percent by weight		Percent	
0-210	0.94	Ash	2.33	SSF 29.7
210-235	2.19	H	7.13	
235-270	5.75	C	85.55	
270-300	7.59	N	1.40	
300-310	2.50	S	.40	
310-355	11.78	O	3.20	
Total boiling < 355°C.	30.75			

[1] AWPA (American Wood Preservers Association).

Tar Acid Fraction

Comparison of results obtained on model compounds when extraction of tar acids was carried out with 10 percent aqueous alkali and Claisen's alkali showed the latter to be much more effective for the extraction, particularly, of high-boiling tar acids. For this reason, Claisen's alkali was used in the separation of the tar acids.

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[99] Unpublished work by E. O. Woolfolk.

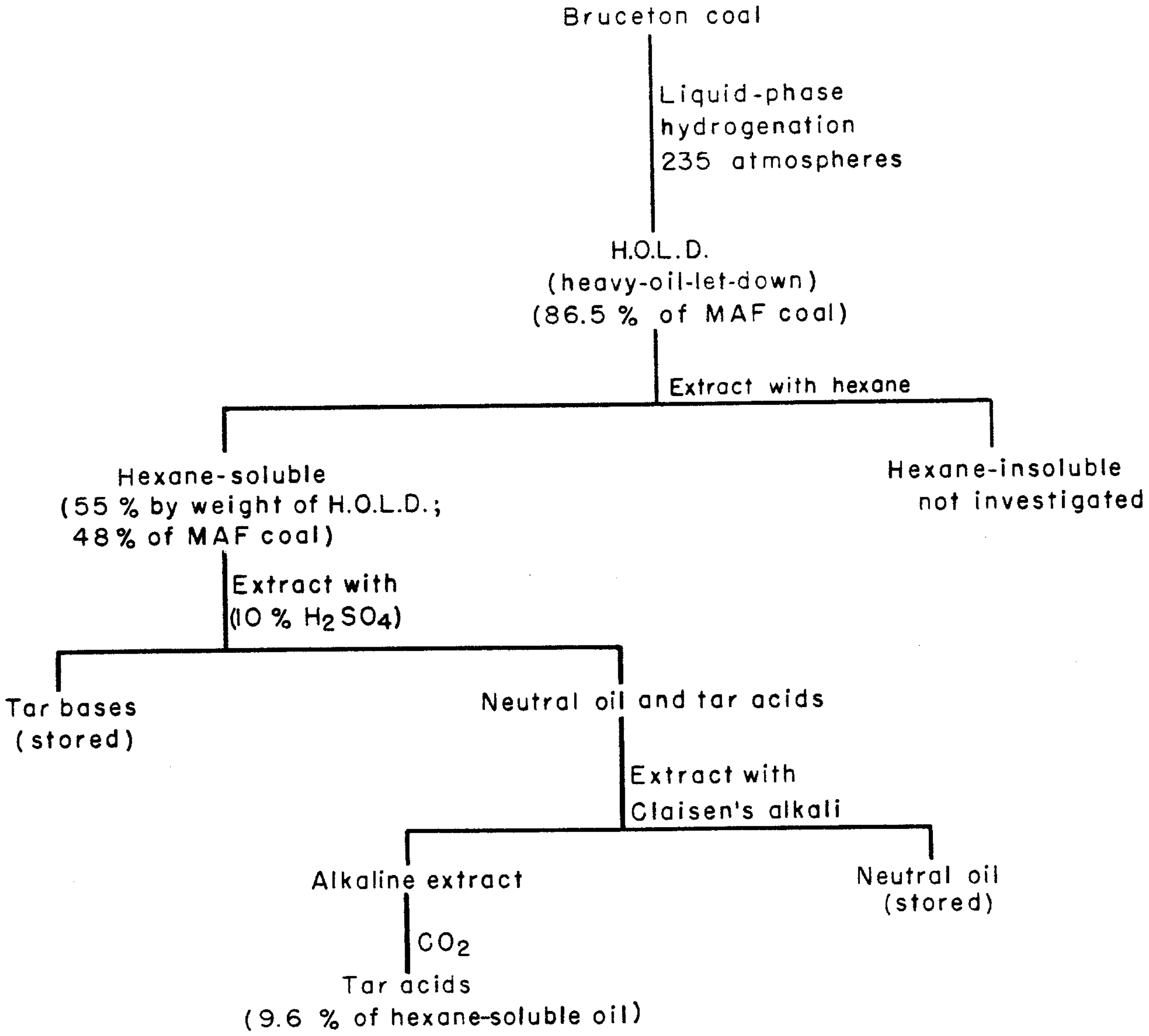

Figure 6.— Schematic diagram of heavy oil product from high-pressure hydrogenation of Bruceton coal.

MAF = Moisture - and ash-free

The crude tar acid fraction recovered from the alkaline extraction represented 9.6 percent by weight of the hexane-soluble oil. Of this, 63.5 percent by weight was obtained by rough distillation at 2.5 mm. Hg to 180°C. end point. The distillable fraction was subjected to precise distillation in vacuo (40 and 30 mm.) in a 3-foot, 25-mm. I.D. Podbielniak column operating at about 25 theoretical plates efficiency. Total recovery was 97 percent. An estimate of the composition of the distillable tar-acid fraction based upon the distillation curve is shown in table 29. About 56.5 percent of the distillate material (35.9 percent of total tar acids) consisted of monohydroxy benzene derivatives boiling below 235°C. (at 760 mm.).

TABLE 29. - Estimated composition of tar-acid fraction in heavy oil from hydrogenated Bruceton coal

(estimated from distillation)

Boiling range, °C. at 40 mm. Hg	Fractions collected	Probable constituents	Percent by volume of total charge	Percent hexane-soluble material
66.5 - 97.5	1 - 3	Solvent	1	
97.5 - 101	4 - 8	Phenol	3	0.3
	[1]19			
101 - 106.5	20 - 25	o-Cresol	4	0.3
108 - 116.5	26 - 43	m- and p- Cresol	14	1
118.5 - 135	44 - 70	C_8 aromatic phenols	23	2
	44 - 47	Probably o-ethylphenol and low-boiling xylenols.		
	48 - 55	Low-boiling xylenols.		
	56 - 62	Middle-boiling xylenols.		
	63 - 70	High-boiling xylenols.		
138 - 145	71 - 82	C_9 aromatic phenols	10.5	0.6
147 - 203	[2]83 -136	These are not ring systems consisting of 2 or more fused aromatic rings	41.5	3
	Residue		3	
			100.0	

[1] Fractions 9-18 put back into still pot.
[2] Fractions 116-136 distilled at 30 mm. Hg.

From data on the quantities of the various constituents isolated and infrared absorption spectra[100] of the fractions collected during precise distillation of the tar acids, an estimate (table 30) was made of the composition of the phenols. The lower-boiling tar acids (below 235° C.) comprised 36 percent of the total tar acids; the higher-boiling, 64 percent. Distribution of the lower-boiling tar acids was as follows: Phenol, 10 percent; cresols, 30 percent; and xylenols and ethylphenols, 60 percent.

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[100] Unpublished work by R. A. Friedel.

TABLE 30. - Composition of phenols in heavy oil from hydrogenated Bruceton coal

Material	Weight percent of total tar acids	Percent of n-hexane soluble oil
Total tar-acid fraction	100	9.6
Distillable fraction[1]	63.5	6.1
Boiling range, <235°C.	35.9	3.4
Phenol	3.6	0.3
Cresols	10.8	1.0
Xylenols and ethylphenols	21.5	2.1
3,5-Dimethylphenol	1.6	0.1
Boiling range, >235°C.	27.6	2.6
3-Methyl-5-ethylphenol	2.0	0.2
Non-distillable fraction	36.5	3.5

[1] 2.5 mm. Hg, 180°C. end point.

Comparison of Results

Comparison of the results of the three investigations of Bruceton coal is difficult, because different procedures were used for isolation and identification of products. Distribution of the lower-boiling tar acids was comparable in the two high-pressure experiments; phenol comprised about 10 percent, cresols 30 to 40, and xylenols, 50 to 60 percent of the tar acids boiling below 235° C. In the low-pressure, low-temperature hydrogenation experiment, more phenol and less xylenols were made. The distribution in this experiment was as follows: Phenol, 25; cresols, 50; and xylenols, 25 percent. The yield of total tar acids on the basis of moisture- and ash-free coal was smaller in the low-pressure test than in the high-pressure tests. In the study of the heavy-oil let-down, tar bases and neutral oil were not investigated. The yields of these fractions were comparable in the other two experiments.