PRODUCTS FROM THE HYDROGENATION OF BRUCETON COAL

Products from Assay Tests

The overhead oil mentioned in row 1 of tables 14 and 17 was further investigated.[83] It was separated into tar acids, tar bases, and neutral oil by extraction with sodium hydroxide and sulfuric acid solutions. Ether or benzene extraction was employed to remove tar acids and bases from the amine sulfate and sodium phenolate solutions, respectively. The yield of tar acids was 17.3 percent and of bases 5.8 percent by volume (19.0 and 6.2 percent by weight).

From distillation curves obtained for the neutral oil, tar acids, and tar bases, it was estimated that about 35 percent of the tar acids was phenol and cresols and about 30 percent was xylenols. Distillation of the lower-boiling tar acids in a more efficient still (90 cm. column packed with glass helices) showed that the phenol fraction, which solidified on standing at room temperature, comprised about 8 percent of the total tar acids. The approximate composition of the tar acids, as indicated by the distillation data, is as follows: phenol, 8 percent; cresols, 27; xylenols, 30; and higher-boiling phenols, 35.

Since most of the tar bases boiled above 190°C., pyridine and its methyl and dimethyl derivatives (picolines and lutidines) were present in comparatively small quantities. Tar bases of high boiling point that were probably present were tri- and tetramethylpyridines, toluidine, indole and its alkyl derivatives, quinoline and its alkyl derivatives, isoquinoline, and naphthylamines.

The neutral oil was similar to the tar bases, in that only a small portion boiled below 200°C. This portion was examined further to obtain an estimate of the benzene, toluene, xylene, naphthenes, and paraffins present. A charge of 790 cc. of neutral oil prepared from the Pittsburgh overhead oil was distilled through a column packed with glass helices over a length of 17 inches. Olefins and aromatics were determined by extracting 5 cc. of oil successively with 85 and 98 percent sulfuric acid. The lower-boiling fractions of the neutral oil contained large portions of saturates. The aromatic content increased with molecular weight (boiling point used as index of molecular weight). The aromatics in the fractions 70° to 100° and 100° to 125°C. were principally benzene and toluene, respectively. Some of the olefins removed by extraction with 85 percent sulfuric acid may have contained aromatic rings (styrene and indene, for example). Refractive-index determinations of the saturated hydrocarbons isolated by extractions with an excess of 98 percent sulfuric acid showed that all fractions of the saturated oil were predominantly naphthenic.

The average fraction of neutral oil boiling below 200°C. (392°F.) was about 27 percent of the total oil yield, and the neutral oil averaged 77 percent of the total overhead oil or oil yield from the coal. Upon the basis of these values, 0.5 gallon of benzene, 0.6 gallon of toluene, and 2 gallons of xylene could be obtained from 1 ton of bituminous coal

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[83] Hirst, L. L., et al., Work cited in footnote 65.

as mined, yielding 170 gallons of oil. From these data, it is evident that commercial quantities of chemical products of higher value than liquid fuel can be obtained in addition to the fuel.

Table 20 shows the distribution of commercially important products and the estimated ultimate yield from Pittsburgh-bed coal hydrogenated under the conditions of the assay tests.

TABLE 20. - Liquid-phase hydrogenation products from Bruceton coal

Substance	Overhead oil, volume percent distilling to 330°C.	Neutral oil volume percent distilling to 207°C.	Estimated ultimate yield	
			Tons per 100 tons m.a.f. coal	Gallons per ton m.a.f. coal
Total tar acids........	17.0		8.94	
Phenol...............	1.4		1.07	
Cresols...............	4.7		3.75	
Xylenols.............	5.2		4.12	
Total tar bases........	4.0		1.76	
Neutral oil:				
Benzene.............	.25	1.58		0.46
Toluene.............	.35	2.11		.64
Xylene..............	1.03	6.26		1.90
Cyclohexane......... Methylcyclohexane....	1.01	6.13		1.86
Dimethylcyclohexane..	.74	4.50		1.36
Tetrahydronaphthalene	2.30	13.90		4.23
High flash naphtha...	10.76	65.60		19.80
Totals to 207° C.	29.0	100.00		-

Oil from Low-Pressure Hydrogenation

In a low-pressure test for the production of heavy oil from Pittsburgh-bed coal, a paste consisting of 1 part powdered coal, 1 to 2 parts heavy recycle oil, and 0.005 part catalyst (mixture of equal parts by weight of tin sulfide and iodine) was pumped with hydrogen at 60 to 70 atmospheres pressure, through a preheater, and then through two converters in series. The first converter had a temperature gradient of 385° to 410° C., and the second had a temperature gradient of 410° to 450° C.[84] The recycle oil consisted of a heavy oil produced from previous operations, which had been centrifuged to remove insoluble material. The approximate retention time of the reactants in the converters was 5 hours. The hydrogen absorption was 5 percent of the weight of coal used. The particular oil investigated was obtained during an 11-day operating period.

[84] Kaplan, E. H., Storch, H. H., and Orchin, M., Hydrogenation and Liquefaction of Coal. Part V. Characterization of Light Oil: Bureau of Mines Tech. Paper 690, 1946, 18 pp.

The products, upon discharge from the second converter, were subjected to rough separation into three fractions: (1) Materials that were gaseous at normal atmospheric conditions; (2) light oil boiling below 250°C.; and (3) a slurry containing oil boiling above 250°C., the ash of the coal, the catalyst, and some unconverted coal. Fraction (3), which was the main product, was called "heavy oil", and, after centrifugation, part of it served as the recycle oil. Heavy oil represented 54 percent of the moisture- and ash-free coal; light oil, 6 percent. It will be recalled that the oil boiling below 270°C. represented about 45 percent of the moisture- and ash-free coal, when hydrogenation was conducted at 200 to 300 atmospheres pressure in a single pass through one converter. Figure 3 (a and b) shows the relative amounts of products obtained.

Light Oil

The light oil, representing about 6 percent of the moisture- and ash-free coal, was fractionated into (1) acidic, (2) basic, and (3) neutral components by extraction with sodium hydroxide and sulfuric acid.85/ Fraction (1) was investigated up to and including the xylenols; (2) up to and including the toluidines; and (3) only in the gasoline range. More than 40 percent of the total light oil boiled above 175°C. The approximate composition of the light oil, estimated from the chemical and physical properties of the fractions obtained by distillation of the preliminary fractions, is summarized in table 21.

TABLE 21 - Composition of light oil from low-pressure
hydrogenation of Bruceton coal

Constituent	Percent of light oil
Tar acids......................................	21.5
Phenol.................................... 2.9	
Cresols................................... 6.6	
Xylenols.................................. 3.3	
Higher tar acids.......................... 1.3	
Loss in extraction and purification....... 7.4	
Tar bases......................................	6.0
Aniline................................... 0.4	
Toluidines................................ .4	
Pyridine bases, b.p. < 200°C. 9	
Higher tar bases.......................... .9	
Loss in extraction and purification....... 3.4	
Neutral oil....................................	72.5
Benzene................................... 0.1	
Toluene................................... 1.0	
Xylenes and ethylbenzene.................. 2.4	
Hydrindene................................ .3	

85/ Fischer, C.H., and Eisner, A., Work cited in footnote 72.

Bruceton coal
Liquid-phase
hydrogenation
60-70 atmos.

Gaseous products

Light oil
(6% of MAF coal)

Heavy oil
(54% of MAF coal)

Extract with
(10% H_2SO_4)

Tar bases
(6% of light oil)
Recoverable tar bases
(3% of light oil)

Neutral oil
and
tar acids
(94% of light oil)

Extract with
(10% NaOH)

Tar acids
(21.5% of light oil)
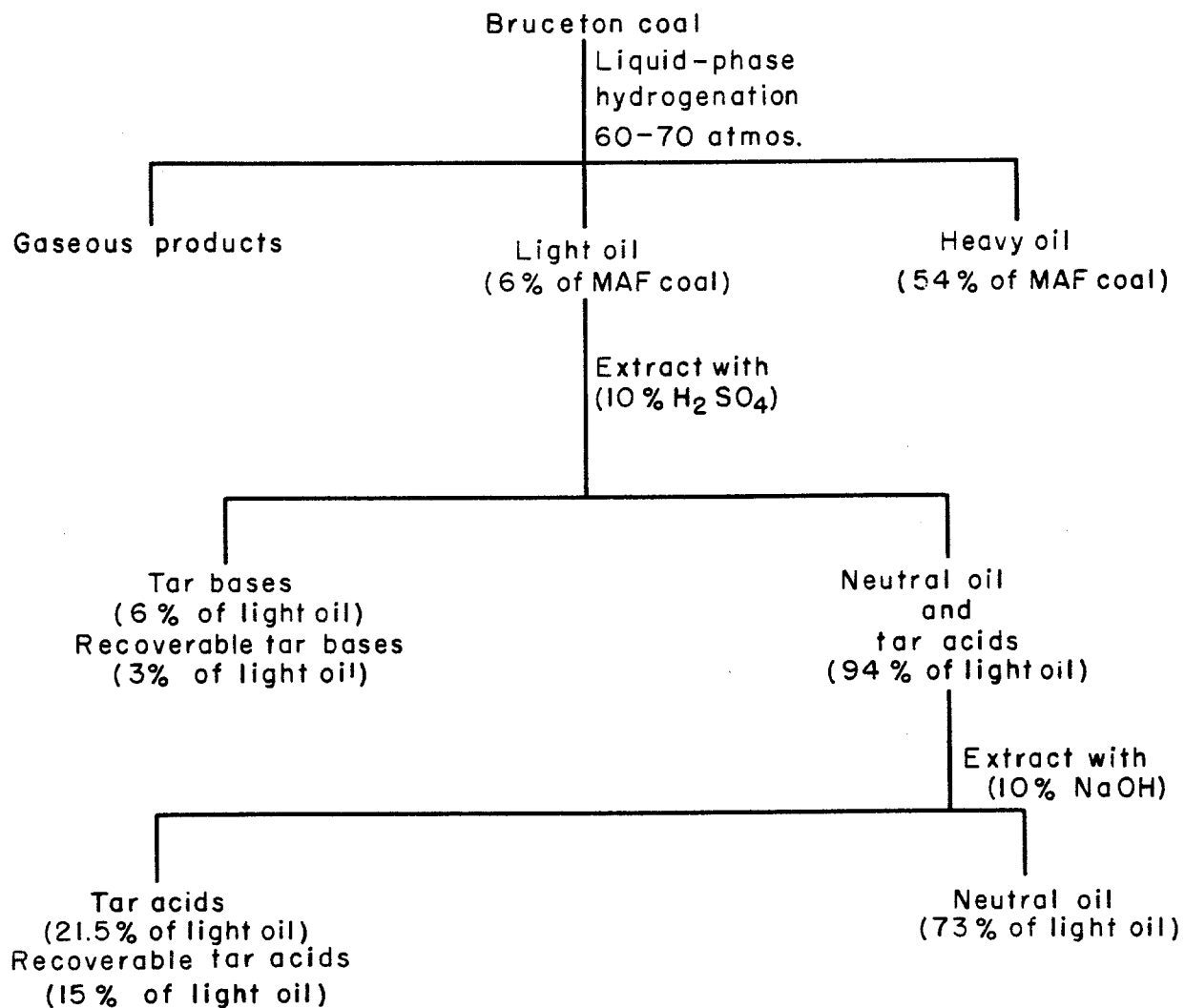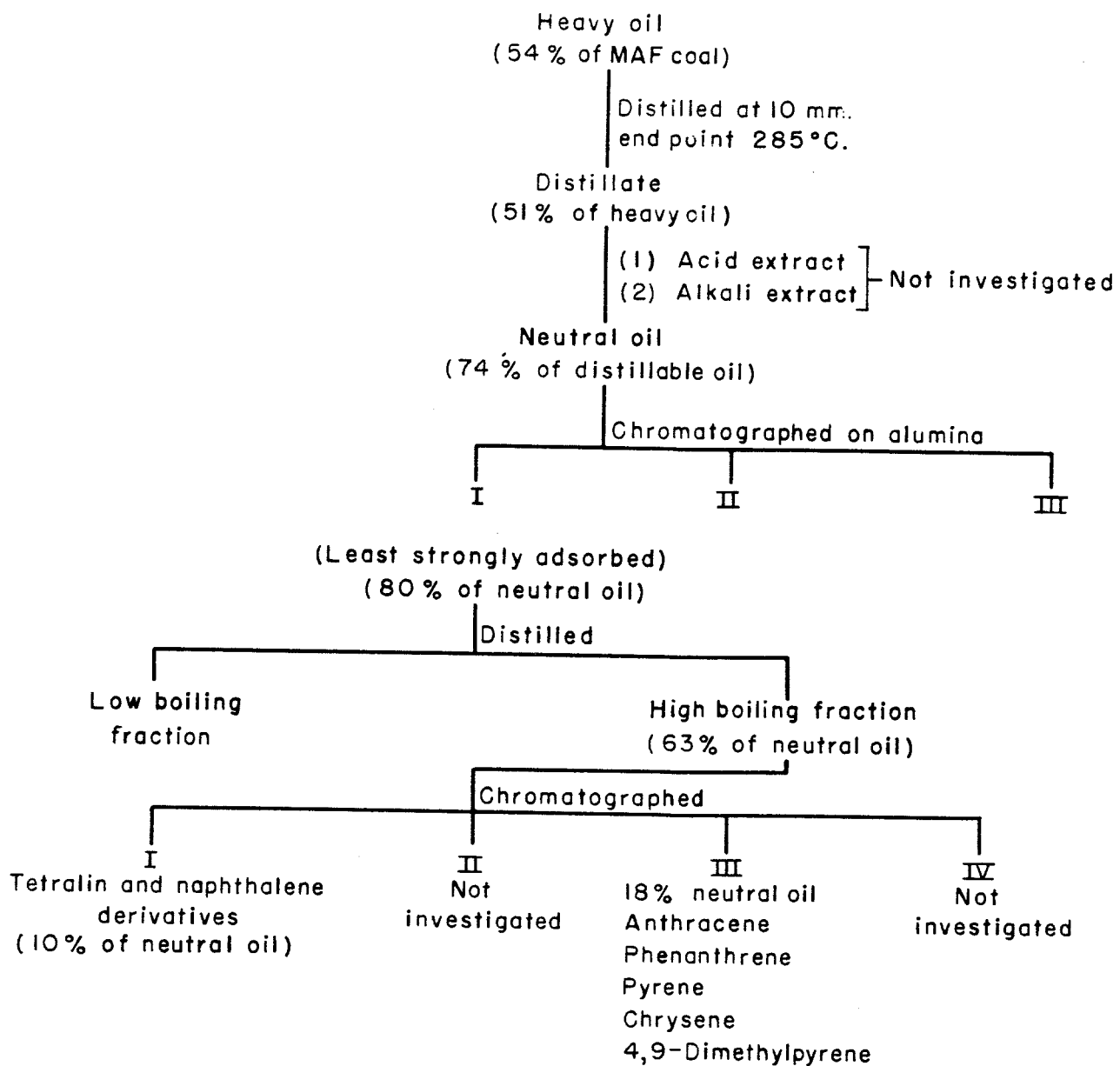Recoverable tar acids
(15% of light oil)

Neutral oil
(73% of light oil)

Figure 3a. — Schematic diagram of products from low-pressure hydrogenation
of Bruceton coal.

MAF = Moisture-and ash-free.

Heavy oil
(54 % of MAF coal)

Distilled at 10 mm.
end point 285°C.

Distillate
(51 % of heavy oil)

(1) Acid extract ⎤
(2) Alkali extract ⎦ — Not investigated

Neutral oil
(74 % of distillable oil)

Chromatographed on alumina

I   II   III

(Least strongly adsorbed)
(80 % of neutral oil)

Distilled

Low boiling   High boiling fraction
fraction   (63% of neutral oil)

Chromatographed

I   II   III   IV
Tetralin and naphthalene   Not   18% neutral oil   Not
derivatives   investigated   Anthracene   investigated
(10% of neutral oil)   Phenanthrene
                                         Pyrene
                                         Chrysene
                                         4,9-Dimethylpyrene

Figure 3b.— Schematic diagram of products from low-pressure hydrogenation
of Bruceton coal.

MAF = Moisture-and ash-free.

TABLE 21 - Composition of light oil from low-pressure hydrogenation of Bruceton coal (Cont'd)

Constituent	Percent of light oil
Other aromatics, b.p.< 178°C.	1.9
Nonaromatics associated with aromatics...	.7
n-Heptane................................	.5
n-Octane.................................	.6
Cyclohexane..............................	1.3
Methylcyclohexane........................	2.0
Dimethylcyclohexanes.....................	.8
Other paraffin hydrocarbons, b.p.<179°C.	3.0
Other naphthenes, b.p.<179° C.	6.3
Neutral oil, b.p.>179°C.	42.2
Distillation losses......................	9.4

Tar Acid Fraction

The tar-acid fraction recovered from the alkaline extraction, and representing 15.2 percent by volume of the light oil, was distilled through a 3-foot column packed with single-turn steel helices. The phenol fraction collected at 182° to 183°C. solidified at room temperature and was color-less. The higher-boiling material was separated into the following three fractions - 183° to 190°, 190° to 200°, and 200° to 233°C. Each fraction was redistilled through the column. This procedure gave relatively pure o-cresol, which crystallized at room temperature. Estimation of the composition of the tar-acid fraction of the light oil (table 22) was made from the distillation curves.

TABLE 22. - Tar acids in light oil from low-pressure hydrogenation

Tar acids	Percent of total tar acids	Percent of phenol through xylenol fraction (col. (2) x 1.20)	Percent by volume of light oil
	(2)	(3)	(4)
Phenol...................................	19	23	2.9
o-Cresol.................................	12	14	1.8
m,p-Cresols..............................	32	38	4.8
Low-boiling xylenols..............	7	8	1.1
2,4-dimethylphenol.................			
2,5-dimethylphenol.................			
Medium-boiling xylenols.............	9	11	1.4
3,5-dimethylphenol................			
2,4-dimethylphenol................			
High-boiling xylenols...............	5	6	.8
3,4-dimethylphenol................			
Acids distilled above 223°C.	1	-	.1
Residue boiling above 228°C.	8	-	1.2
Hold-up and distillation loss........	8	-	1.2
			15.3

The ratio of m- to p-cresol in the meta-para-cresol fractions was determined by means of the method recommended by the British Tar Producers Association.86/ This procedure indicated a content of 55 percent m-cresol and 45 percent p-cresol. The value of 21.5 of tar acids represented the amount of material extracted and included considerable resinous and tarry material. The quantity of recoverable tar acids was 15 percent of the light oil.

The evidence points to about an equal quantity of high-boiling phenols and polyphenols in the heavy oil. For purposes of comparison of distribution of lower-boiling tar acids, the fraction from phenol through the xylenols boiling in the range 180° to 225° C. can be used as a standard. Column (3) of table 22 shows the phenol, cresols, and xylenols calculated to this basis.

Table 23 compares the phenol-through-xylenol fraction produced by the low-pressure hydrogenation of Bruceton coal with the corresponding fraction obtained by low-temperature (500°C.) carbonization of the same coal.87/ Also included are the results reported for the tar-acid fraction obtained from a typical high-temperature carbonization tar and from the high-pressure hydrogenation of Velva lignite.88/

TABLE 23. - Distribution of the tar acids in phenol-through-xylenol range from coal hydrogenation and coal carbonization

	Hydrogenation		Carbonization	
	High pressure, percent	Low pressure, percent	High temperature, percent	Low temperature, percent
Phenol........................	12.8	23	35	3.5
o-Cresol......................	7.5	14	14	10.2
m-, p-Cresols.................	29.5	38	30	31.0
Xylenols......................	50.2	25	21	55.3
m-/p-Cresol...................	.76	1.22	1.31	-

From this table, it appears that the distribution of lower-boiling tar acids - phenol, cresol, and xylenols, - obtained by low-pressure hydrogenation resembles more closely the distribution of the acids from high-temperature carbonization. Coal carbonized at high temperature produces larger quantities of phenol and smaller quantities of xylenols than coal

86/ Standardization of Tar Products Test Commission, Standard Methods for Testing Tar and its Products: 2nd ed., 1938, p. 234.
87/ Fieldner, A. C., Davis, J. D., Brewer, R. E., Selvig, W. A., Reynolds, D. A., and Sprunk, G. C., Carbonizing Properties and Petrographic Composition of Pittsburgh-Bed Coal from Bureau of Mines Experimental Mine, Bruceton, Allegheny County, Pa.: Bureau of Mines Tech. Paper 594, 1939, 43 pp.
88/ Industrial and Engineering Chemistry, Hydrogenation of Coal. A Round-Table Discussion: Vol. 36, 1944, p. 291.

carbonized at low temperature, probably as a result of thermal splitting of alkyl groups from the benzenoid nucleus of the alkylated phenols at higher temperatures. It has been shown[89] that an increase in the carbonization temperature produces a decrease in the total quantity of tar acids and an increase in the quantity of aromatic material. This probably results in part from the loss of the oxygenated function from polyalkylated phenols. These conclusions are in accord with the experiments of Cawley[90] who found that cresols at 450°C. under hydrogen pressure and in the absence of cata- lyst were both deoxygenated and demethylated to a small extent, and that at 500°C. both processes occurred to a greater extent. Cawley also found that the presence of a catalyst increased the deoxygenation reaction enormously and affected the demethylation reaction to only a minor extent. From the present study it is apparent that considerable phenol and cresol survive the low-pressure catalytic hydrogenation treatment, and that probably con- siderable demethylation of xylenols took place. Of course, the tar acids during coal hydrogenation are in an environment totally different from that which prevails when pure cresol is hydrogenated, and constituents in the ash of the coal may affect the rate and type of reaction. It recently has been shown[91], for example, that small quantities of alkali increase the rate of hydrogenation of certain cresols, and other work has shown that the course of the hydrogenation of some phenols can be changed by alkali. Also, in a comparison of distribution of tar acids, the fractionating effective- ness of the distillation column is an important factor, and caution should be exercised in comparing results obtained with different columns.

Tar Base Fraction

The tar bases were distilled in one operation through a 3-foot column packed with single-turn steel helices. Estimation from the distillation curve of the composition of this fraction resulted in the values shown in table 24.

TABLE 24. - Distribution of tar bases

	Percent of total tar bases	Percent of light oil
Pyridine bases, b.p. < 200°C.	34	0.9
Aniline............................	16	.4
Toluidines........................	14	.4
Residue...........................	36	.9
		2.6

[89] Fieldner, A. C., and Davis, J. D., Gas-, Coke-, and By-Product-Making Properties of American Coals and Their Determination: Bureau of Mines Monograph 5, 1934, 164 pp.

[90] Cawley, C. M., Hydrogenation of Cresols and Dihydric Phenols: Fuel, vol. 12, 1933, p. 29.

[91] Ungnade, H. E., and Nightingale, D. V., The Effect of Bases on the Hydro- genation of Alkylphenols in the Presence of Raney Nickel: Jour. Am. Chem. Soc., vol. 66, 1944, p. 1218.

A portion of the aniline fraction was acetylated with acetic anhydride in aqueous solution. The acetanilide formed was isolated in 92-percent yield, based upon the weight of aniline fraction used for the acetylation; it had a melting point of 113° C. (Literature reports 113° to 114° C.) The toluidine fraction, similarly acetylated, gave a 55-percent yield of aceto-toluidides. The value of 6 percent of tar bases included resinous and tarry material; the quantity of recoverable tar bases was 3 percent of the light oil.

Neutral Oil Fraction

The unextracted portion (72.5 percent by volume of the light oil) remaining after treatment of the light oil with acid and alkali was neutral oil. Distillation through a 6-inch column indicated that its boiling range was 65° to 295° C. and that most of the material boiled between 100° and 250° C.

The crude neutral oil was distilled roughly, and the fraction boiling below 175° C. was collected; this represented less than half of the total distillate. The fraction boiling above 175° C. was not investigated. Dispersion measurements on the lower-boiling fraction indicated the presence of about 39 percent aromatics. Ultimate analysis gave 12.7 percent hydrogen and 87.2 percent carbon, indicating that the material was hydrocarbon in nature and contained no appreciable quantity of oxygen-containing compounds.

Separation into type compounds was effected by the Bureau of Standards method[92][93] involving selective adsorption on activated silica gel. This utilizes the property of aromatic compounds to adsorb more strongly than paraffins or naphthenes on silica gel. If a judicious ratio of silica gel to oil is used, aromatics are retained on a column of silica gel, and the paraffins and naphthenes are washed through the column by means of a volatile paraffin solvent, such as pentane or isopentane. The presence of olefins in the neutral oil hinders the separation into aromatic and non-aromatic fractions; hence, the neutral oil was first hydrogenated with Raney nickel under such conditions that no aromatics were reduced. After separation, the aromatic and nonaromatic fractions were each distilled through an efficient fractionating column.

[92] Mair, B. J., and Forziati, A. F., Separation and Recovery of Aromatic Hydrocarbons from Paraffins and Naphthenes by Adsorption: Nat. Bureau of Standards Jour. Research, vol. 32, 1944, p. 165.

[93] The separation of aromatics from paraffins and naphthenes was carried out with 50-ml. batches of mildly hydrogenated neutral oil boiling below 175° C. This oil was poured through a column of 350 grams of activated silica gel contained in a glass tube 2.5 cm. in diameter and about 100 cm. high. The adsorption tube was water-jacketed, as was the calibrated receiver used to catch the percolate. Each 25 ml. of percolate was examined separately. When the 50 ml. of oil had passed onto the silica gel, 250 ml. of pentane was added to elute the paraffins and naphthenes. This was followed by 400 ml. of absolute methanol, which eluted the aromatic fraction.
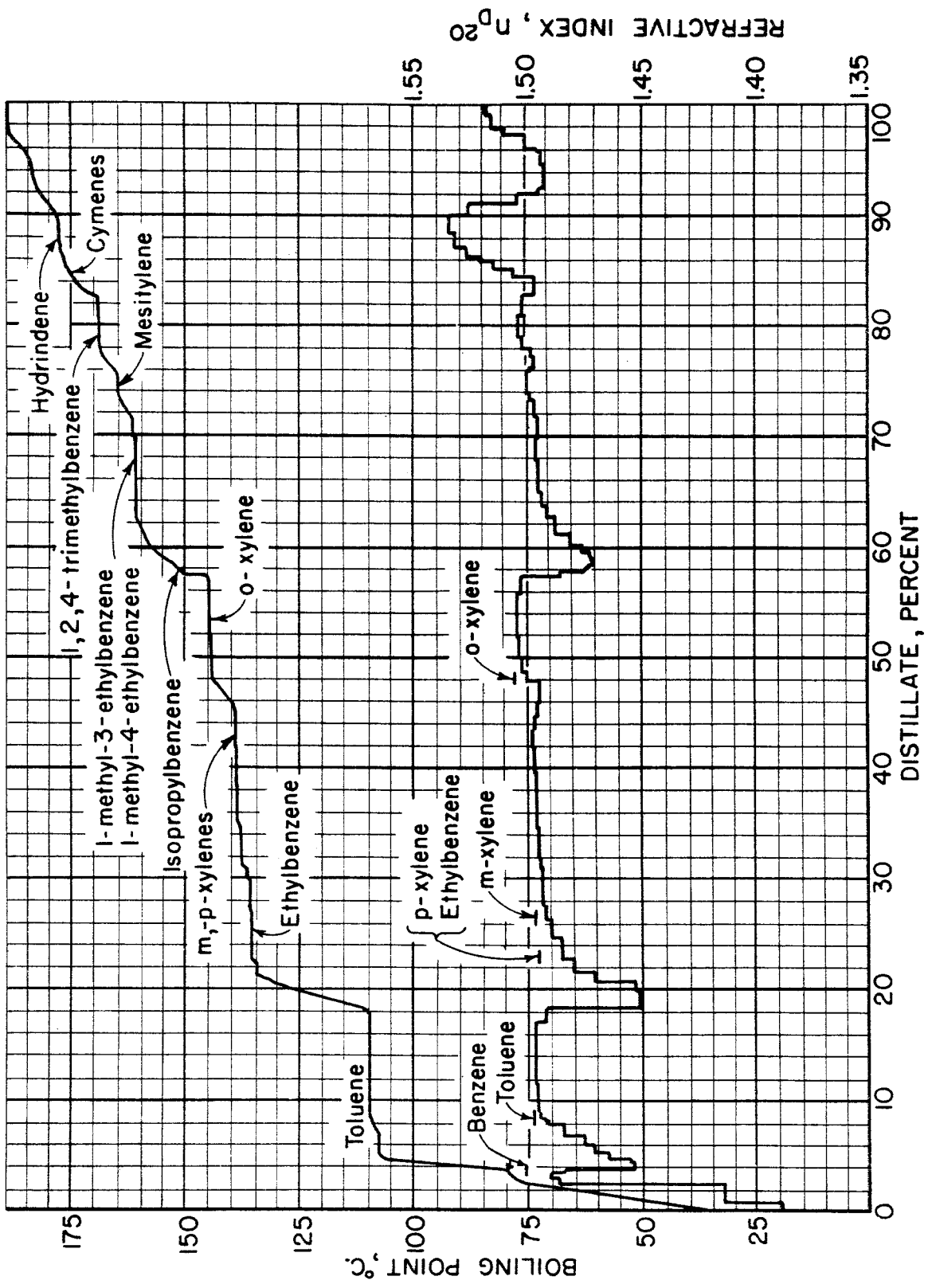
Figure 4. – Precise distillation of aromatic fraction of neutral oil (~175°C.) from low-pressure hydrogenation of Bruceton coal.

Hirst analyzed for olefins and aromatics contained in neutral oils by sulfuric acid extraction. This method of analysis tends to change the nature of the constituents of the oil, since sulfuric acid catalyzes alkylation and polymerization reactions. These difficulties can be avoided by using chromatographic adsorption for the separation of aromatic and nonaromatic material.

Aromatic fraction. - Distillation of the aromatic fraction through a commercial, 6-foot, high-temperature, Podbielniak heli-grid column [94] produced the distillation curve shown in figure 4. Combination, on the basis of boiling temperature and refractive index, of the 84 fractions collected resulted in 33 fractions. Analysis of each fraction included the determination of density, index of refraction, and specific dispersion.[95] From the physical constants and analytical data, approximate proportions of the various components of the aromatic portion of the neutral oil were estimated and are shown in table 25.

TABLE 25. - Composition of aromatic fraction (12.5 percent of neutral oil), Percent by volume

	Percent of aromatic fraction	Percent of total neutral oil	Percent of light oil
Benzene.......................	1.4	0.2	0.1
Toluene........................	11.2	1.4	1.0
Ethylbenzene...................	7.5	1.0	0.6
m-,p-xylenes..................	12.1	1.5	1.0
o-Xylene......................	9.7	1.2	.8
Isopropylbenzene.............	1.4	.2	.1
1-Methyl-3-ethylbenzene ⌐ 1-Methyl-4-ethylbenzene _⌐····	9.8	1.2	.8
1-Methyl-2-ethylbenzene ⌐ Mesitylene _⌐····	3.9	.5	.3
1,2,4-Trimethylbenzene.......	4.3	.5	.4
Cymenes ⌐ 1,2,3-Trimethylbenzene ⌐··· 1,2-Diethylbenzene _⌐	4.1	.5	.4
Hydrindene......	3.3	.4	.3
Butylbenzene ⌐ 1,4-Diethylbenzene ⌐ 1-Methyl-3-propylbenzene ⌐·· 1-Methyl-4-propylbenzene_⌐	4.3	.5	.4
1,2-Dimethyl-4-ethylbenzene..	3.2	.4	.3
Non-aromatics (by difference)	8.7	1.1	.7
Residue, b.p.>189°C.	15.2	1.9	1.3
		12.5	8.5

[94] Performance tests with this column, using a methylcyclohexane-heptane test mixture at a reflux rate corresponding to that employed for the distillation of the aromatic fraction, indicated that the column had a theoretical plate value of 70 plates at total reflux. The relative volatility figure of 1.082 for the heptane-methylcyclohexane mixture given by Griswold (Griswold, J., Pure Hydrocarbons from Petroleum: Ind. and Eng. Chem., vol. 35, 1942, p. 247) was used in this calculation. A reflux ratio of about 150 was used in the distillation of the aromatic fraction.

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

Benzene was present in very small quantity and toluene, ethylbenzene, and xylenes in larger quantities. An appreciable quantity of nonaromatic material, probably olefins that escaped hydrogenation, was present in the aromatic portion.

There are several interesting facts about table 25. First is the random distribution of the compounds. The physical constants of the aromatic fractions indicated that nearly all the alkylated benzenes were probably present, except those with long side chains. The small quantity of benzene present is also of interest. It is possible that much of the benzene was selectively hydrogenated to cyclohexane during hydrogenation of the coal, but this seems unlikely, since so much other aromatic material survived the hydrogenation process. It seems unlikely that the original coal substance contains unsubstituted benzene rings. The benzene that is present in oils from high-pressure hydrogenation of coal probably is a secondary product resulting from dealkylation and dehydroxylation. The presence of considerable quantities of hydrindene is also of interest. It would appear that the indene structure occurs as such in the coal substance, and some of the polynuclear compounds obtained by coal hydrogenation and carbonization may result from the polymerization of indene.

Paraffin-naphthene (nonaromatic) fraction. - The portion of the neutral oil containing paraffins and naphthenes was distilled through the 6-foot Podbielniak column. In view of the large number of possible compounds in this material, it was subjected to a rough distillation through the 6-foot column, and the distillate was divided into eight fractions. The first fraction was then redistilled separately through the column until about 80 percent of the material had distilled. Distillation was interrupted, and the second fraction was added to the residue. This process was repeated for each fraction. The distillation curve was continuous and is shown in figure 5. The density and index of refraction for each fraction are also included in this figure. The specific dispersions of the fractions indicated the absence of aromatics or olefins in the distillate.

Analysis by infrared absorption spectra of several of the lower-boiling fractions showed a predominance of naphthenes. Table 26 shows the distribution of products in the fractions studied by infrared analysis. Identification by this method of the constituents in the whole nonaromatic fraction of the neutral oil was hindered by a lack of the spectra of reference compounds.