

PRODUCTS FROM HYDROGENATION OF COAL

RESULTS OF BUREAU OF MINES ASSAYS OF TYPICAL UNITED STATES COALS

The Bureau of Mines conducted a program of liquid-phase coal-hydrogenation assays in a small, continuous, experimental plant to obtain information regarding the amenability to hydrogenation of the various types of coals that exist in the United States and the factors governing the relative amounts and characteristics of the oils produced.

Assay Procedure

In the assay procedure, a mixture of about equal parts of powdered coal and heavy oil was pumped with hydrogen under 200 to 300 atmospheres into the converter (a vertical alloy-steel tube 3 inches I.D. by 8 feet long)

heated to 430° to 450°C. 60/61/62/63/64/65/66/67/68/ The contact time and temperature were varied until a maximum yield of "overhead" oil (oil obtained by condensation of the oil vapors carried out of the top of the converter by the stream of hydrogen) was obtained. A heavy oil slurry in which were suspended the ash of the coal, the unreacted coal, and the catalyst particles, was discharged through a standpipe about 6 feet above the bottom of the converter. This slurry was centrifuged, and the resulting oil was mixed with another charge of coal and catalyst. For each coal assayed, the first generation of paste was made with a foreign vehicle, such as a suitable fraction of low-temperature coal tar or heavy oil from the hydrogenation of a previously tested coal. Subsequent generations of paste were made with the heavy oil from the preceding generation as vehicle. Thus the assay consisted essentially in determining the optimum conditions for the maximum yield of oil consistent with complete regeneration of the vehicle used in making a paste with the original coal.

The assay product consisted of about 20 to 30 percent by volume of light oil boiling in the gasoline range (to 205°C.), 70 percent of middle oil (205° to 330°C.), and 10 percent of heavy oil (over 330°C.). About 77 percent of the total overhead oil or oil yield from the coal was neutral oil, which

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- 60/ Storch, H. H., Hirst, L. L., Fisher, C. H., and Sprunk, G. C., Hydrogenation and Liquefaction of Coal. Part I. Review of Literature, Description of Experimental Plant, and Liquid-Phase Assays of Some Typical Bituminous, Subbituminous, and Lignitic Coals: Bureau of Mines Tech. Paper 622, 1941, 110 pp.
- 61/ Hirst, L. L., Eisner, A., Field, J. H., Cooper, H. M., Abernethy, R. F., and Storch, H. H., Hydrogenation and Liquefaction of Coal. Part III. Characterization of Assay Oils: Bureau of Mines Tech. Paper 646, 1942, 27 pp.
- 62/ Fieldner, A. C., Storch, H. H., and Hirst, L. L., Bureau of Mines Research on the Hydrogenation and Liquefaction of Coal and Lignite: Bureau of Mines Tech. Paper 666, 1944, 69 pp.
- 63/ Storch, H. H., and Fieldner, A. C., Coal Hydrogenation, U. S. Bureau of Mines Experimental Plant: Mech. Eng., vol. 61, 1939, pp. 605-611.
- 64/ Hirst, L. L., Hawk, C. O., Sprunk, G. C., Golden, P. L., Pinkel, I. I., Boyer, R. L., Schaeffer, J. R., Kallenberger, R. H., Hamilton, H. A., and Storch, H. H., Liquid-Phase Hydrogenation of Pittsburgh Seam Coal: Ind. and Eng. Chem., vol. 31, 1939, pp. 869-877.
- 65/ Hirst, L. L., Storch, H. H., Fisher, C. H., and Sprunk, G. C., Hydrogenation of High-Volatile Bituminous Coals; Proximate Analysis and Characterization of Products: Ind. and Eng. Chem., vol. 32, 1940, pp. 864-871.
- 66/ Hirst, L. L., Storch, H. H., Fisher, C. H., and Sprunk, G. C., Hydrogenation and Petrography of Subbituminous Coals and Lignites: Ind. and Eng. Chem., vol. 32, 1940, pp. 1372-1379.
- 67/ Storch, H. H., Hirst, L. L., Golden, P. L., Pinkel, I. I., Schaeffer, J. R., and Kallenberger, R. H., U. S. Bureau of Mines Experimental Plant: Ind. and Eng. Chem., vol. 29, 1937, pp. 1377-1380.
- 68/ Hirst, L. L., Boyer, R. L., Eisner, A., Pinkel, I. I., and Storch, H. H., Hydrogenation of High-Volatile Bituminous Coals. Summary of Assays of Bituminous Coals, Subbituminous Coals, and Lignites: Ind. and Eng. Chem., vol. 33, 1941, pp. 1068-1072.

contained 10 percent olefins, 54 percent aromatics, and 36 percent saturates. The saturates consisted of approximately equal parts of naphthenes and paraffins. About 20 percent of the total overhead oil consisted of tar acids and about 3 percent of tar bases.

Thirteen coals representative of the geographical distribution of coals in the United States and ranging in rank from high-volatile A bituminous coal to lignite were assayed. The yields obtained under the optimum conditions by hydrogenation for each coal are presented in table 13.^{69/} The coals are arranged in order of the total carbon content of the dry, ash-free coal, the highest carbon content being at the top of the table and the lowest at the bottom. This arrangement places the coals in order of rank, with the highest rank at the top of the table.

Characterization of Assay Oils

Summary of Data for 13 Coals Assayed

The factors governing the characteristics of the oils produced in the liquid-phase hydrogenation of coals may be classified in two groups, the first being those related to the rank and type of coal and its chemical and petrographic composition, and the second being the operating variables, such as the temperature, pressure, time of contact, catalyst, and amount and temperature of refluxing of the overhead oil before it leaves the converter. A study of the results of the numerous runs under various operating conditions for each of the 13 coals assayed showed that the operating variables, and especially the reflux temperature, had a much greater effect upon the characteristics of the overhead oils than did the rank, type, and composition of the coal.

Effect of Rank

The yield of oil based upon percentage of dry, ash-free coal (column 13, table 13) in general decreased with decrease in rank below that of the West Virginia coal. The lowest yield in coals of high-volatile bituminous rank was 62 percent for the Alabama (Sayreton mine) coal, and the highest yield was 74 percent for the Utah (Columbia mine) coal. The other six high-volatile bituminous coals gave oil yields between 69 and 71 percent, inclusive. The Alabama (Sayreton mine) coal would be expected to give the lowest yield of the high-volatile group because it is of distinctly higher rank than the others, verging on medium-volatile; likewise, the Utah (Columbia mine) coal would be expected to give the highest oil yield because of its relatively low position in the high-volatile rank and its high content of resin, which hydrogenates readily. On the same moisture- and ash-free basis, the three subbituminous coals gave lower oil yields, ranging from 62 to 67 percent, and the two Dakota

^{69/} Fieldner, A. C., and Hirst, J. L., Work cited in footnote 62.

lignites the lowest yields - 54 and 55 percent. However, in actual practice, the oil yields based upon coal as mined or washed are progressively lower than the above results on account of the increasing moisture content of the low-rank coals. Lignites contain 35 to 45 percent moisture.

Column 17 of table 13 gives the oil yields in gallons per ton of coal as mined. This is the crude oil from the assay tests. The total average yield of gasoline obtainable from this crude, including vapor phase hydrogenation of the middle oils, is estimated at 70 percent of the oil yields given in columns 13 and 17. None of these yields includes the coal or other fuel required for the generation of additional hydrogen, steam, and power. Usually, this additional coal is estimated as equal to the coal liquefied, so that the net yields of liquid fuel per ton of total coal used for all purposes should be taken as one-half of the yields given in table 13.

For the high-volatile bituminous, subbituminous, and lignitic coals, average yields were 20, 24, and 25 percent of gas and 10, 13, and 15 percent of water, respectively. The increase in yield of water with decrease in rank was not as large as would have been expected if all the oxygen of the coal substance in excess of its hydrogen equivalent to form water had combined with hydrogen in the liquefaction process. It was shown in the research with the small autoclaves that much of the oxygen of subbituminous coals and lignite was evolved as oxides of carbon, especially carbon dioxide. This conclusion is supported further by evidence from the hydrogen-consumption values of column 12 of table 13. The lignites absorbed somewhat less hydrogen than the high-rank coals.

The only characteristic measurably influenced by the composition of the coal was the percentage of tar acids, which tended to increase as the rank decreased.^{70/} No systematic variation in tar-base yield with rank of coal or with boiling range of the oil fractions was observed. The yield of tar acids and tar bases was about 10 times that obtained in coal carbonization. The lower-rank coals, including lignite, subbituminous coal, and high-volatile C bituminous coal, yielded 12 to 16 percent of tar acids on the basis of the moisture- and ash-free coal. The higher-rank coals yielded 5 to 15 percent of tar acids. High-volatile B and C bituminous coals gave the largest yields of tar acids in pounds per ton of coal as mined or washed. The highest yields were 269 and 258 pounds, respectively, from the Washington (Strain-Upper Diamond mine) and Illinois (Orient No. 2 mine) coals. The Wyoming subbituminous coal also gave a high yield of 219 pounds. The average percentages of tar acids by volume in the overhead oils were 15, 24, and 26, respectively, for high-volatile bituminous, subbituminous, and lignite coal. Although these figures are subject to considerable variation with changes in operating conditions of the liquefaction process, they show that the products of coal hydrogenation constitute an important potential source of raw materials for plastics.

^{70/} Hirst, L. L., et al., Work cited in footnote 61.

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TABLE 13.- Liquefaction yields for optimum conditions of hydrogenation.

Origin of coal: State and mine or town	Rank	Con- verter temper- ature, °C.	Pressure, lb. per sq. in.	Catal- yst ^{1/2}	Paste pumping rate, lb./hr.	Ratio, oil: heavy oil	Yields, as percent of dry, ash-free coal			As percent of dry, ash-free coal				Oil yield, gal./ton coal ^{1/3} mined ^{1/4}	
							Gas	water- soluble products	Or- ganic solids	Hydro- gen ab- sorbed	Hydro- gen ab- sorbed	Aro- matic oil	Tar acids, yield		Tar bases, yield
Alabama, Sayreton	1	430	4,000	5	7.23	0.7	26	7	10	57	6	33	8	2.5	136
West Virginia, I.C.C. No. 21	2	450-460	4,500	1	7.2	0.5	28	5	2	62	11	69	5	2.0	156
Alabama, Empire	2	454	4,500	2	7.2	0.5	20	3	2	62	12	73	8	1.7	176
Pennsylvania, Experimental	1	440	3,200	1	7.1	0.4	19	11	4	66	9	74	11	2.8	169
Utah, Columbia	2	440	3,300	2	7.2	0.3	13	12	6	69	7	74	11	2.6	170
Illinois, Orient No. 2	1	427	3,300	1	8.24	0.8	15	12	6	66	8	71	15	1.7	155
Indiana, Saxton No. 1	2	450	3,300	2	7.2	0.5	20	10	6	64	9	70	12	3.3	141
Washington, Strain-Upper Diamond	1	425	3,300	1	8.4	0.2	20	13	2	65	8	70	15	3.7	155
Montana, Colstrip	2	433	4,600	1	7.25	0.4	20	15	7	58	8	63	14	2.1	108
Colorado, Puritan	1	436	3,300	2	6.15	0.8	24	13	6	57	10	63	13	2.8	115
Wyoming, Monarch No. 45	2	430	4,600	2	8.7	0.4	26	10	3	61	8	66	16	3.1	123
North Dakota, Beulah	1	425	3,300	1	6.0	0.8	25	14	11	50	7	54	12	1.6	79
North Dakota, Velva	2	439	4,500	2	8.8	0.4	25	16	8	51	7	55	15	1.6	79

1/ BHVA - Bituminous high-volatile A; BHVB - bituminous high-volatile B; BHVC - bituminous high-volatile C; SSB - Subbituminous B; Lig - lignite.
 2/ Catalyst 1 is 0.5 percent SnS and 0.5 percent MoO₃; catalyst 2 is 0.1 percent SnS and 0.05 percent CH₃. These percentages are based upon weight of coal charged to converter.

3/ Time of contact, 2.2 hours.

4/ Time of contact, 1.8 hours.

5/ Time of contact, 2.5 hours.

6/ Distilling up to 330°C.

7/ Calculated as follows:

$$\text{Col. 13} \times (100 - (\text{percent moisture} + \text{percent ash})) \times 20 \\ 100 \times 0.94 \times 8.35$$

In this formula, percent moisture and ash is on the basis of coal as mined or washed; 20 is 1 percent of weight of ton, in pounds; 0.94 is average specific gravity of oil; 8.35 is weight of 1 gallon of water.

Column 14 of table 13 shows that, with a few exceptions, the total aromatic neutral oil, in percentage of moisture- and ash-free coal, increased regularly with increasing rank of coal from 22 percent (of the moisture- and ash-free coals) for lignites to 41 percent for high-volatile A bituminous coal. This spread would be 13.5 to 37.5 percent when based upon the coals as mined. These oils constitute about half of the total oil yield and can serve as good stock for the preparation of high-octane aviation fuel. The yield of olefins ranged from 3 to 6 percent and that of saturates from 12 to 24 percent of the moisture- and ash-free coals.

The percentage of olefins in the neutral oils showed a slight tendency to increase as the rank of coal decreased. However, these changes were much smaller than those produced by changes in the reflux temperatures in the converter by different runs on the same coal.

Effect of Operating Variables

The distillation data show that an average of 27 percent of the overhead oils distill in the gasoline range up to 200° C. (392° F.), 64 percent between 200° and 330° C. (392° and 626° F.), and 9 percent above 330° C. (626° F.). The specific gravities of the overhead oils and of the various fractions are higher than those of the corresponding petroleum products owing to the presence of large proportions of aromatic hydrocarbons, tar acids, and tar bases.

One-half to two-thirds of the total tar acids boiled below 235° C. and comprised phenol, cresols, and xylenols. Of the tar acids boiling above 235° C., about 55 percent boiled in the range 235° to 270° C., 28 percent between 270° and 300° C., and 17 percent in the 300° to 330° C. range.

The principal constituent of all the fractions of overhead oil was neutral oil. The high average of aromatics (54 percent) indicated a reasonably good octane value for gasoline made from these oils. The percentages of olefins and saturates averaged 10 and 36, respectively. The saturates consisted of approximately equal parts of naphthenes and parafins.

Results of Special Analyses on Products from Certain Typical Coals

Properties of Selected Overhead Oils

Samples of the product oils from certain typical coals collected when the plant was operating under conditions considered optimum for liquid-phase liquefaction were subjected to special analysis.^{71/} In contrast to the coals used, the overhead oils were similar in composition. The moisture- and ash-free coals contained 73 to 84 percent carbon; the oils ranged in carbon content from 85 to 87 percent.

^{71/} Storch, H. H., et al., Work cited in footnote 60.

Data obtained from distillation of the specially selected samples in 6-inch indented columns of the Vigreux type showed that 30 percent or less of the overhead oil boiled below 188° C. Most of the oil distilled at 188° to 300° C.; comparatively little boiled above 330° C. The specific gravity of the fractions was high, owing to the presence of large amounts of aromatic hydrocarbons, tar acids, and tar bases. The fractions boiling in the range 188° to 207°C., 207° to 235°C., and 235° to 270°C. probably would be satisfactory wood-preserving oils. Table 14 summarizes the distillation data.

The overhead oils were extracted with sulfuric acid and sodium hydroxide solutions, according to the method of Fisher and Eisner,^{72/73/} to remove tar acids and tar bases. The residue was neutral oil.

Tar Acids and Tar Bases

The data on tar acids can be used in estimating the amounts of phenol, cresols, xylenols, and higher phenols present, since the fractions were collected according to the boiling points of these tar acids (table 14).

^{72/} Fisher, C. H., and Eisner, A., Determination of Tar Acids and Bases by Extraction Methods: Ind. and Eng. Chem., anal. ed., vol. 9, 1937, pp. 213-218.

^{73/} Since only traces of carboxylic acids and polyhydric phenols were usually present, a preliminary wash with potassium carbonate solution instead of sodium chloride was employed in making the correction for water absorption. Probably the greatest error in the determination of tar acids and bases was caused by sludging and resin formation. Addition of 20 percent sulfuric acid (saturated with sodium chloride) after the removal of tar acids caused much resin to form. Less sludging occurred when about 5 percent hydrochloric acid was used at this stage instead of sulfuric acid, and higher values for tar bases were obtained. For this reason, the tar-base values are probably low.

TABLE 14. - Distillates from special samples of overhead oils

No. of oil	Origin of coal	Distilling range, °C.					
		20-188	188-207	207-235	235-270	270-300	300-330
<u>Percent by volume of overhead oil (total)</u>							
1	Pennsylvania, Bruceton.	20.1	9.6	18.5	21.3	16.9	8.5
1A	Pennsylvania, Bruceton.	16.5	9.2	15.4	20.2	16.5	12.9
2	Illinois.....	17.7	6.0	10.6	14.9	11.3	13.8
3	Washington.....	18.1	5.7	11.8	17.6	18.6	17.8
4	Montana.....	25.3	5.3	12.0	14.8	14.3	14.4
5	Colorado.....	20.9	7.6	13.8	21.2	14.8	14.2
6	North Dakota, Beulah...	19.3	6.4	15.1	20.8	13.1	13.4
7	North Dakota, Velva....	22.0	13.4	16.7	25.3	14.8	7.2
7A	North Dakota, Velva....	30.0	6.9	19.9	25.5	12.9	3.2
<u>Specific gravity at 15.6°C.</u>							
1	Pennsylvania, Bruceton.	0.849	0.953	0.965	0.977	0.998	1.013
1A	Pennsylvania, Bruceton.				.984		1.028
2	Illinois.....	.814	.944	.958	.965	.977	.977
3	Washington.....	.808	.942	.956	.967	.981	.994
4	Montana.....	.809		.950	.960	.973	.987
5	Colorado.....	.821	.949	.960	.967	.979	.994
6	North Dakota, Beulah...	.805	.931	.958	.969	.982	.993
7	North Dakota, Velva....	.829	.954	.967	.977	.985	1.001
7A	North Dakota, Velva....	.831		.961	.972	.977	
<u>Tar acids, percent by volume of overhead-oil fraction</u>							
1	Pennsylvania, Bruceton.	14.8	34.0	29.4	20.8	12.0	13.0
1A	Pennsylvania, Bruceton.	17.6	33.5	26.8	16.4	9.2	7.5
2	Illinois.....	12.6	39.0	37.3	27.0	17.0	14.5
3	Washington.....	7.6	38.0	37.5	25.4	15.2	10.0
4	Montana.....	9.8	41.0	40.5	32.0	21.0	11.5
5	Colorado.....	11.4	39.3	38.6	27.6	18.4	12.8
6	North Dakota, Beulah...	11.2	38.5	40.8	32.5	21.2	13.8
7	North Dakota, Velva....	16.0	45.5	47.0	34.8	23.0	15.2
7A	North Dakota, Velva....	8.6	43.8	45.9	36.4	22.0	18.5
<u>Tar bases, percent by volume of overhead-oil fraction</u>							
1	Pennsylvania, Bruceton.	5.6	8.5	5.6	4.2	4.0	4.5
1A	Pennsylvania, Bruceton.	3.8	7.5	5.6	5.6	3.6	5.0
2	Illinois.....	3.8	4.5	2.8	2.0	4.0	1.0
3	Washington.....	4.8	9.0	7.5	5.0	3.0	3.0
4	Montana.....	4.6	5.2	2.5	2.5	4.0	4.0
5	Colorado.....	5.3	8.0	4.4	5.2	3.0	2.2
6	North Dakota, Beulah...	3.8	5.0	3.2	3.3	2.8	3.6
7	North Dakota, Velva....	4.0	2.0	3.0	4.4	3.5	4.8
7A	North Dakota, Velva....	5.4	2.8	3.6	3.6	4.0	1.0

In table 15, the concentration and yield of tar acids as volume percent of fraction of overhead oil and weight percent of moisture- and ash-free coal, respectively, are shown for several coals. Low-temperature tar produced at temperatures up to about 750°C. contains large amounts of tar acids, but the proportion boiling in the phenol, cresol, and xylenol range is comparatively low. These facts indicate that, although conducted at a lower temperature than low-temperature carbonization, hydrogenation plays a definite part in lowering the molecular weight of tar acids.

In table 16, the tar-acid and tar-base yields are compared with the oxygen and nitrogen contents of the parent coals. There is an apparent trend toward increase in tar-acid yield with decreasing rank (or increasing oxygen content of the moisture- and ash-free coal) and in tar acids boiling below 235°C., with the exception of Bruceton coal, which has a high concentration of phenols, cresols, and xylenols. The higher yield of tar acids from the Velva lignite, as compared with the Beulah lignite, was due to the larger yield of overhead oil as well as the higher concentration of tar acids in this oil. Possibly these differences resulted from the different catalyst and higher hydrogen pressures used for the Velva lignite. The yield of neutral oil distilling below 330°C. was very sensitive to the reflux temperatures. This, combined with the variations due to the rank of the coal, accounts for the somewhat erratic variations in the last column of table 16.

Neutral Oil

The principal constituent of all the fractions from the overhead oils was neutral oil. The oxygen content of neutral oil from North Dakota lignite was exceptionally high - 3.35 percent. It has been observed that a portion of the oxygen of the neutral oils is present as peroxides. Ether and ring oxygen probably account for most of the oxygen content. The nitrogen in the neutral oil is doubtless contained in bases of high molecular weight that are not readily soluble in acid.

Owing to the absence of tar acids and tar bases, the specific gravity of the neutral oil was lower than the specific gravities of the original overhead-oil fractions. Table 17 shows separation of the neutral oil into olefins, aromatics, and saturates by means of a modification of the Kester and Pohle method.^{74/75/} Neutral oil was extracted with 85 percent sulfuric acid to determine olefins; aromatics were determined by extraction of the "olefin-free" oil with 98 percent sulfuric acid. The sulfuric acid method roughly indicates the aromatic and saturates present and usually yields low values for the content of saturates because of the solubility of branched-chain paraffins in 98 percent sulfuric acid.

^{74/} Kester, E. B., and Pohle, W. D., Determination of Olefin, Aromatic, and Paraffin Hydrocarbons in Neutral Oil from Coal Tar: Ind. and Eng. Chem., anal. ed., vol. 3, 1931, pp. 294-297.

^{75/} Fisher, C. H., and Eisner, A., Graphic Analysis of Hydrocarbon Oils: Ind. and Eng. Chem., anal. ed., vol. 9, 1937, pp. 366-370.

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TABLE 15. - Concentration and yield of tar acids

(as volume percent of fraction and weight percent of moisture- and ash-free coal, respectively)

Oil No.	Coal	O ₂ , percent	Boiling range, °C.						Yield to 235°C.	Boiling range, °C.			
			20-188		188-207		207-235			235-270	270-300		
			Concentration	Yield	Concentration	Yield	Concentration	Yield		Concentration	Yield		
1	Pennsylvania, Bruceston	6.8	15.5	1.77	36.3	2.61	28.0	3.10	7.48	17.5	2.32	11.0	1.38
2	Illinois.....	10.0	12.6	1.57	39.0	1.87	37.3	2.77	6.21	27.0	1.28	17.0	1.36
3	Washington.....	12.5	12.0	1.48	38.0	1.48	37.5	3.03	5.99	25.4	3.05	15.2	1.93
4	Montana.....	16.2	10.0	1.22	44.0	2.97	44.0	4.20	8.39	33.0	3.70	23.5	1.92
5	Colorado.....	16.4	13.5	1.64	43.1	1.82	39.5	4.13	7.59	29.0	3.74	21.0	1.64
6	North Dakota, Beulah..	19.4	8.6	0.91	38.5	1.32	40.8	3.40	5.63	32.5	3.70	21.2	1.51
7	North Dakota, Velva....	21.4	12.8	1.73	44.5	2.31	46.5	4.40	8.44	35.6	4.68	22.5	1.62

TABLE 16. - Tar acids and tar bases from special samples of overhead oils, compared with oxygen and nitrogen contents of parent coals

Oil No.	Coals	Overhead oil distilling to 330°C., (percent, by volume) ^{1/}		Overhead oil distilling to 235°C., percent by volume	Moisture- and ash-free coal (percent by weight)					
		Tar acids	Tar bases		Oxygen	Nitro- gen	Overhead oil to 330°C. acids	Tar bases	Neutral oil	
1	Pennsylvania, Bruceton	17.0	4.3	11.3	6.8	1.7	65.2	11.1	2.8	51.3
2	Illinois.....	21.7	3.0	8.5	10.0	1.9	52.4	11.4	1.6	39.4
3	Washington.....	21.2	5.2	8.0	12.5	2.1	61.4	13.0	3.2	45.2
4	Montana.....	22.7	3.1	9.6	16.2	1.1	55.0	12.5	1.7	40.8
5	Colorado.....	20.9	4.5	10.7	16.4	1.6	58.2	12.2	2.6	43.4
6	North Dakota, Beulah..	23.4	2.6	10.9	19.4	1.0	48.5	11.4	1.3	33.8
7	North Dakota, Velva...	30.2	3.0	17.4	21.4	1.0	55.0	16.5	1.7	36.8

^{1/} In calculating percent by weight of moisture- and ash-free coals, using analytical percent-by-volume data, no allowance was made for differences in density. Such corrections should be fairly uniform, hence the comparative conclusions should be valid.

TABLE 17 - Neutral oil distillates from special samples of overhead oils

Oil No.	Origin of coal	Fractions, °C.					
		20-188	188-207	207-235	235-270	270-330	300-330
<u>Neutral oil fractions</u> (percent by volume of neutral oil distilling to 330°C.)							
1	Pennsylvania, Bruceton.	22.6	7.8	17.0	22.6	20.1	9.9
1A	Pennsylvania, Bruceton.	18.5	7.7	14.8	22.3	20.5	16.2
2	Illinois.....	26.5	6.0	11.5	19.0	16.0	21.0
3	Washington.....	23.2	4.4	9.5	17.8	22.3	22.8
<u>Olefins (percent by volume of neutral-oil fraction)</u>							
1	Pennsylvania, Bruceton.	6.0	3.0	3.0	7.0	7.0	14.0
1A	Pennsylvania, Bruceton.	8.0	5.4	5.4	8.8	10.6	13.2
2	Illinois.....	8.0	4.0	5.0	12.0	9.0	11.0
3	Washington.....	10.4	7.8	7.6	7.6	16.0	12.8
4	Montana.....	7.2	7.0	6.0	7.0	9.6	13.6
5	Colorado.....	8.4	7.8	6.4	8.6	13.0	15.8
6	North Dakota, Beulah...	18.0	14.0	10.5	10.0	13.0	15.5
7	North Dakota, Velva....	12.8	11.0	8.0	7.0	7.0	12.5
7A	North Dakota, Velva....	13.6	8.6	8.8	7.6	8.6	11.8
<u>Aromatics (percent by volume of neutral-oil fraction)</u>							
1	Pennsylvania, Bruceton.	30.0	66.0	79.0	78.0	84.0	76.0
1A	Pennsylvania, Bruceton.	36.6	70.6	80.6	77.8	75.4	69.6
2	Illinois.....	22.0	52.8	65.6	70.4	83.0	86.0
3	Washington.....	19.2	45.6	58.0	66.0	64.0	59.4
4	Montana.....	16.8	47.0	58.4	66.0	71.0	70.4
5	Colorado.....	20.4	48.8	60.2	63.0	62.0	58.8
6	North Dakota, Beulah...	17.3	51.0	58.0	68.5	80.0	68.5
7	North Dakota, Velva....	21.6	50.8	66.0	71.4	74.2	70.5
7A	North Dakota, Velva....	16.4	49.0	60.8	69.2	71.2	68.7
<u>Saturates (percent by volume of neutral-oil fraction)</u>							
1	Pennsylvania, Bruceton.	64.0	31.0	18.0	15.0	9.0	10.0
1A	Pennsylvania, Bruceton.	55.4	24.0	14.0	13.4	14.0	17.2
2	Illinois.....	70.0	43.2	29.4	17.6	8.0	3.0
3	Washington.....	70.4	46.6	34.4	26.4	20.0	27.8
4	Montana.....	76.0	46.0	35.6	27.0	19.4	16.0
5	Colorado.....	71.2	43.4	33.4	28.4	25.0	25.4
6	North Dakota, Beulah...	64.5	35.0	31.5	21.5	7.0	16.0
7	North Dakota, Velva....	65.6	38.2	26.0	21.6	18.8	17.0
7A	North Dakota, Velva....	70.0	42.4	30.4	23.2	20.2	19.5

The composition of the neutral oil varied greatly with boiling point. The olefin content decreased at first with increase in molecular weight and then increased. Simple olefins of high molecular weight are rather

inactive to sulfuric acid; possibly the olefin linkages in the higher fractions of neutral oil are activated by conjugation with aliphatic or aromatic double bonds.76/77/

The aromatic content increased with molecular weight and then decreased slightly, with one exception, namely, the Illinois neutral oil. Aromatic hydrocarbons predominated in all of the fractions boiling above 188°C. The fraction that boiled at 20° to 188° C. contained 15 to 37 percent aromatics and 55 to 76 percent saturates. This fraction is interesting as a source of gasoline, solvents, and hydrocarbon chemicals.

The saturated oils remaining after several extractions with an excess of sulfuric acid had comparatively low refractive indices, indicating the presence of considerable amounts of paraffin hydrocarbons. The paraffinic content was estimated by comparing the refractive indices and boiling points with those of known hydrocarbons.78/ The first fraction contained, on the average, about 0.5 ring per molecule; therefore, this fraction was about 50 percent paraffins. The higher fractions contained 0.8 or 0.9 ring per molecule, and the average molecule may be pictured as alkyl cyclohexanes. Probably the paraffins present are mainly of the branched-chain type. In view of the highly cyclic structure usually attributed to coal, it is interesting to note that the content of paraffins corresponds to about 10 percent of the moisture- and ash-free coals. For the higher fractions of saturates, the production of naphthenes with only one ring from highly cyclic materials would require the rupture of two or three rings.

Since the refractive index changes considerably with boiling point for saturates boiling below 200°C., an attempt was made to avoid the errors that might result from this fact by distilling the first fraction (boiling up to 188°C.) into the following six fractions: 20°-70°C., 70°-100°C., 100°-125°C., 125°-150°C., 150°-175°C., and 175°-191°C. From the data obtained, it appears that, on the average, all the low-boiling fractions contain about 0.5 ring per molecule for the Washington (bituminous high-volatile C coal) coal and about 0.7 ring for the bituminous high-volatile A coal. For the first four fractions, the presence of dicyclic naphthenes can be excluded on the basis of boiling points. Therefore, the first four fractions should contain about equal amounts of cyclohexane or cyclopentane derivatives and paraffin hydrocarbons.

76/ Brooks, B. T., and Humphrey, I., The Action of Concentrated Sulfuric Acid on Olefins, with Particular Reference to the Refining of Petroleum Distillates: Jour. Am. Chem. Soc., vol. 40, 1918, pp. 822-856.

77/ Norris, J. F., and Joubert, J. M., The Polymerization of Amylenes: Jour. Am. Chem. Soc., vol. 49, 1927, pp. 873-886.

78/ McArdle, E. H., Moore, J. C., Terrell, H. D., and Haines, E. C., Composition of High-Solvency Hydrocarbon Thinners: Ind. and Eng. Chem., anal. ed., vol. 11, 1939, pp. 248-250.

In another study, the neutral oils were distilled through a 60-inch packed column of about 50 theoretical plates and the fraction boiling below 225° C. was investigated.^{79/80/} On the distillation curve, plateaus were apparent at about 80°, 100°, 110°, 120°, 175°, and 210° C.

Comparison of the values for different coals indicated no trend with rank of the parent coals in the oils boiling below 225°C. Similarly, the data for olefin, aromatic, and saturates content indicated no trend with rank in the boiling range below 225°C.

From density, refractive index, and sulfuric acid-solubility data it was concluded that between 50 and 90 percent of all of the oil fractions boiling below 200°C. and 20 to 50 percent of those boiling above 200°C. were insoluble in 98 percent sulfuric acid and apparently consisted mainly of naphthenic compounds - alkylcyclopentanes, alkylcyclohexanes, and alkyldecyclodecanes (saturated alkylhydronaphthalenes). In the 50° to 85° fractions, the presence of large portions of branched hexanes, cyclopentane, methylcyclopentane, and cyclohexane was apparent. The fractions boiling below 150°C., that were insoluble in 85 percent sulfuric acid but soluble in 98 percent, contained large amounts of branched-chain paraffins and naphthenes, as well as benzene, toluene, and xylenes. The fractions boiling above 150°C., that were soluble in 98 percent but insoluble in 85 percent acid, contained only a small proportion of paraffinic or naphthenic hydrocarbons; the main components were benzene and naphthalene homologues.

An analysis is reported by Gordon^{81/} of the hydrocarbon products obtained from the hydrogenation of creosote oil during the manufacture of aviation gasoline. The composition of the C₄-C₇ fractions is shown in table 18. A product similar in composition would be obtained, if coal were the starting material.

^{79/} Hirst, L. L. et al., Work cited in footnote 61.

^{80/} The packed section (0.79 inch or 2.0 cm. in diameter, 60 inches or 152 cm. in length) of the still was filled with stainless-steel rings of 3/22-inch (2.4-mm.) inside diameter. According to previously reported tests, the height equivalent to a theoretical plate for this packing is about 1.1 inch (2.8 cm.). Two liters of oil was distilled from the 3-liter still reservoir with a reflux ratio of about 9:1, maintained by an automatic reflux still head.

^{81/} Gordon, K., Hydrogenation in Fuel and Chemistry Industry: Jour. Inst. Fuel, vol. 21, 1948, pp. 53-61.

TABLE 18. - Analysis of hydrocarbons produced during the hydrogenation of creosote oil

		Percent
C ₄ fraction:	Iso-butane.....	71
	n-Butane.....	29
C ₅ fraction:	Iso-pentane.....	83
	n-Pentane.....	12
	Cyclopentane.....	5
C ₆ fraction:	Benzene.....	12.5
	Cyclohexane.....	8
	Methyl cyclopentane.....	40.5
	Methyl pentanes.....	33
	n-Hexane.....	6
C ₇ fraction:	Toluene.....	18
	Methyl cyclohexane.....	40
	Dimethyl cyclopentane.....	22
	Methyl hexanes.....	20
	n-Heptane.....	1

Heavy (Recycle) Oil

Data pertaining to heavy (recycle) oils discharged from the bottom of the converter are given in table 19.^{82/} Data for centrifuged Washington heavy oil also are included. These oils contain more carbon, nitrogen, and sulfur and less hydrogen and oxygen than the corresponding overhead oils. The heavy oil with the highest nitrogen content came from the coal (Washington) that was richest in nitrogen. The carbon:hydrogen ratios were lower than those of the original coals but higher than those of the overhead oils. Although produced from coals that have a wide range of properties, the heavy oils were similar, the carbon and hydrogen contents being, respectively, 88.2 to 89.5 percent and 6.8 to 7.4 percent.

TABLE 19. - Data for heavy (recycle) oils

Coal	Percent by weight								C/H ratio
	Insoluble matter		Ash content	Ash-free basis					
	Total	Or-ganic		Hydro-gen	Carbon	Nitro-gen	Oxy-gen	Sulfur	
Pennsylvania...	17.0	10.1	6.9	6.8	89.5	1.4	1.6	0.7	13.2
Illinois.....	17.5	7.6	9.9	7.4	89.1	1.1	1.7	.7	12.0
Washington.....	11.9	5.0	6.9	7.4	88.7	2.0	1.5	.4	12.0
Washington ^{1/} ...	9.6	4.5	5.1	7.4	88.6	2.0	1.7	.4	12.0
Colorado.....	21.8	10.5	11.3	7.1	89.5	1.4	1.5	.5	12.6
North Dakota...	32.1	17.4	14.7	6.9	88.2	1.0	3.3	.6	12.8

^{1/} After centrifuging.

^{82/} Storch, H. H., et al., Work cited in footnote 60.