Characterization of Components in Low-Temperature Lignite Tar

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AS DESCRIBED BY Batchelder (*1*), primary tar from the low-temperature carbonization of lignite can be processed in many different ways. The various products obtainable contain a wide assortment of chemicals and classes of chemicals in different combinations. The major effort of this work was directed toward identifying the classes of the chemicals in primary tar rather than searching out the identities and quantities of individual components.

The most important characteristic of low-temperature tar is that usually, for each class of compounds found, all the homologs are present. However, no one compound is present in a large amount. In the primary tar, as received, phenol is the most abundant single compound, at about 1%.

PRIMARY TAR

Primary tar is composed of materials that distill at temperatures from below 100° to about 350° C., as well as high-molecular-weight, pitchlike materials. All characterization work has been done on distillates. However, it is believed that the residual material has the same general proportions of chemical compound classes as do the distillable fractions.

Primary tar is composed of tar acids, tar bases, and neutral oil as determined by their relative solubility or insolubility in caustic or dilute acid. The solvent-extraction process (*1*) divides the primary tar so that most of the tar acids are soluble in the methanol-water phase, and most of the neutral oil is soluble in the hexane phase; the tar bases are divided evenly between the two phases.

Figure 1 shows the boiling point, refractive index, and density curves obtained from a vacuum fractional distillation of a vacuum-flash distillate of primary tar. The individual fractions were composited to 15 fractions. All of these, except for the lowest boiling composites, contained about the same proportions of tar acids, tar bases, and neutral oil. The fall in refractive index and corresponding rise in density have not been explained or studied. These effects might have resulted from azeotrope formation, because neither tar acids nor neutral oil showed this effect when they were distilled separately. The average composition of distillates of lignite tar is as follows: tar acids, 25 to 30%; tar bases, 4 to 5%; neutral oil, 65 to 70%.

TAR ACIDS

Tar acids were primarily phenolic compounds with no more than 2% of aliphatic carboxylic acids. For this work, tar acids were divided into low-boiling and high-boiling tar acids. The dividing atmospheric boiling point was 235° C., as this temperature is slightly higher than the 225° C. boiling point of the least volatile xylenol (*3*, *4*), and thus ensured the inclusion of all the xylenols in the low-boiling tar acids. The separation was generally made by distilling off the low-boiling tar acids under vacuum in a nitrogen atmosphere. The high-boiling tar acids were sometimes distilled at temperatures up to those equivalent to 300° to 350° C. at atmospheric pressure; in such cases, only about 50 to 60% of the high-boiling tar acid fraction distilled.

Low-Boiling Tar Acids. The composition of the low-boiling tar acids was studied by infrared spectroscopy after the acids had been converted to their methyl ethers by the method of Rowe and Bannister (*6*). The conversion to methyl ethers minimized the possibility of ambiguities due to thermal and oxidative effects and had several advantages from an infrared point of view. The methyl ethers, obtained from the tar acids in a yield of 95%, were fractionally distilled through a Podbielniak Hypercal column at reflux ratios of 20/1 to 40/1 at atmospheric pressure under nitrogen. The individual fractions were examined by infrared, although in some cases a number of fractions could be combined. The analytical absorption bands, base line locations, and absorption coefficients used for these determinations will be reported elsewhere. Unexpected ketonic materials were detected by infrared in the material distilling between the plateaus corresponding to the methyl ethers.

Table I shows the tar-acid composition based on this analysis. By calculation, the primary tar contained about 0.8% of phenol, the most abundant single tar acid.

High-Boiling Tar Acids. Crude tar acids were obtained from vacuum distillate of primary tar by caustic extraction. The crude acids were distilled under vacuum to obtain a

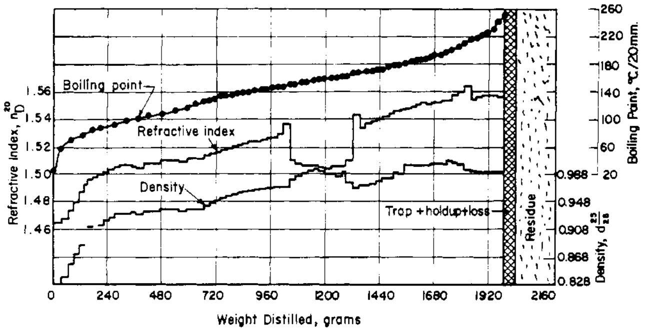

Figure 1. Fractionation by distillation of vacuum-flash distillate

Table I. Composition of C_6 through C_8 Tar Acids as Calculated from Infrared Analysis of their Methyl Ethers

Compound	Relative Amounts of Isomers of Each Type of Tar Acid, Wt. %	Concentration of Each Tar-Acid Isomer in Respect to Total Amount of Tar Acids Identified, Wt. %	
Phenol	100	2	
Cresols			
2-Methylphenol	29	13	44
3-Methylphenol	39	17	
4-Methylphenol	32	14	
Xylenols			
2,3-Dimethylphenol	12	3	18
2,4-Dimethylphenol	32	6	
2,5-Dimethylphenol	19	3	
2,6-Dimethylphenol	5	1	
3,4-Dimethylphenol	14	2	
3,5-Dimethylphenol	18	3	
Ethylphenols			
2-Ethylphenol	17	2	11
3-Ethylphenol	32	3	
4-Ethylphenol	51	5	

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rough cut (b.p. 200 to 335° C. at 1 atm.), which was finally distilled at reduced pressures through a packed column to yield 18 fractions.

Each fraction was studied by a variety of conventional experimental methods. These included absorption chromatography, paper and gas partition chromatography, nonaqueous titrations to determine average equivalent weights, infrared spectroscopy, mass spectroscopy, and specific color reactions to identify certain classes of phenolic compounds. The types of compounds identified by these techniques are shown in Table II. No one class of tar acids was predominant, and the presence of the various classes of compounds varied with the boiling range being studied. In general, the alkyl side chains appeared to consist primarily of methyl and ethyl groups. Ketonic contaminants were found in all of the fractions studied. Based on determinations with hydroxylamine hydrochloride, the concentration of ketones in each fraction ranged generally from 6 to 12%.

TAR BASES

Tar bases are present in tar distillates to the extent of about 4%. As they represent a small part of the tar, only limited studies were made of their nature. Actually, all of the tar bases cannot be easily recovered, and yields of less than 1.5% were realized by conventional recovery methods. Distillations, spot tests, and paper chromatography indicated that tar bases are primarily nitrogen heterocyclics of the pyridine and quinoline types. No evidence was obtained for aniline derivatives.

NEUTRAL OIL

Neutral oil, which represents more than two thirds of primary tar, is principally hydrocarbons: paraffins, olefins, and aromatics. Also present are nonacidic "polar compounds" which contain oxygen, sulfur, or nitrogen. Figure 2 shows the results of fractionating neutral oil in a Podbielniak Hypercal unit. Evidence of some degree of separation is shown by the plateau in the boiling point curve and the periodic rise and fall of the refractive index curve. Infrared studies of selected fractions showed those corresponding to the maxima of the refractive index curve to be predominantly aromatic, and those corresponding to the minima to be predominantly aliphatic. The periodicity is evidence for the homologous nature of the chemicals in primary tar.

Table II. Classes of Compounds Identified in High-Boiling Tar Acids

1. Alkylphenols with total number of alkyl carbon atoms from 3 to 6
2. Catechol, resorcinol, and hydroquinone and their alkylated derivatives
3. Trihydric phenols (probably a small quantity)
4. Indanols and alkylated indanols
5. Napthols and alkylated napthols
6. Higher molecular weight polynuclear phenols
7. Ketones (appeared in all 18 distillation fractions of high-boiling tar acids)
8. Indenols and acenaphthols were tentatively identified by mass spectrography in addition to classes noted above

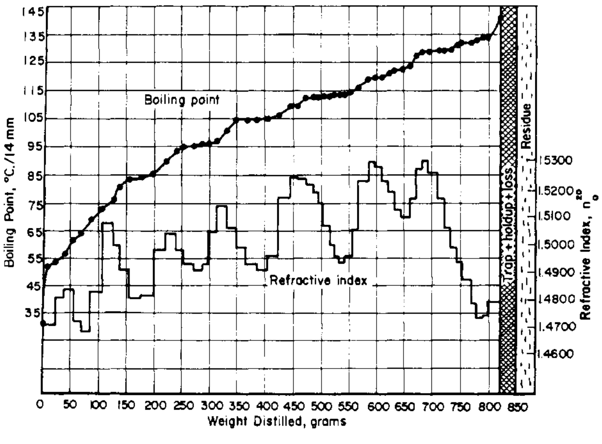

Figure 2. Precision fractionation of neutral oils

Silica gel-displacement chromatography was used to assay neutral oil for content of paraffins, olefins, and aromatics. Figure 3 shows a typical curve obtained by the method in which cyclohexanol was used as the "pusher" or the displacement solvent (*3, 4*). These results are compared in Table III with those obtained by a conventional sulfuric acid extraction method (*5*). There is no entirely satisfactory explanation for the remarkable differences in the paraffin and aromatic values. However, the polar compounds, which are believed to be present in about 20%, could be the cause of difference. They are classed as "aromatics" by the silica gel method being displaced after the aromatics and before the displacement solvent, but as olefins in the sulfuric acid method.

The various classes of compounds in neutral oil have been separated and studied for the types of structures present. Infrared spectroscopy has been the chief analytical technique used for identification of structural features.

Paraffins. The paraffins in lignite tar are primarily straight-chain hydrocarbons with a small amount of branching. The location of the branching is not known, but is probably random. About one third of the paraffins form an adduct with urea. This indicates either that the adducted paraffins are unbranched or that the branching is close to the end of the hydrocarbon chain. Hydrocarbon ring analysis based on physical properties showed that the paraffins and olefins combined contain about 20% ring carbon atoms.

Paraffins were isolated from high-boiling fractions of neutral oil as colorless waxes. Although considerable efforts were made to purify these waxes to yield high-melting solids, the highest melting point range attained was 40° to 47° C. Infrared and elemental analyses of these waxes showed them to contain only carbon and hydrogen.

Olefins. Early infrared studies on selected olefins fractions, separated from neutral oil by silica gel, showed the three

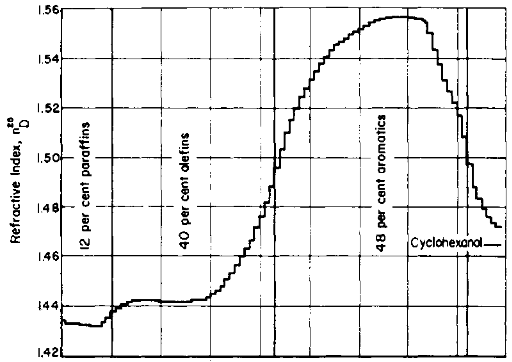

Figure 3. Silica gel adsorptogram for neutral oil

Table III. Composition of Neutral Oil

Component	Method of Analysis	
	H_2SO_4	Silica Gel
Paraffins	33	11–13
Olefins	43	35–40
Aromatics	24	48–53

major kinds of olefins present to be terminal or alpha, trans-internal, and tertiary.

To learn more about the olefins, the effect of various strengths of sulfuric acid on the removal of olefins was studied. Figure 4 shows how the percentage of neutral oil extracted rises as stronger sulfuric acid is used, a sharp rise taking place at 70% acid. At this acid strength, the bromine number of the acid-treated material begins to drop rapidly. The material extracted by the more dilute acids is believed to be mostly polar compounds. Figure 5 shows a silica gel curve of neutral oil washed with 78% sulfuric acid. The proportion of olefins remaining in the treated material was slightly higher than in the original neutral oil. The actual presence of olefins in fraction 25 was verified by infrared. Table IV shows the calculated amounts and the proportions of the paraffins, olefins, and aromatics that were extracted by the acid.

About half of the olefins present in lignite tar are α-olefins. Because the double bond is located at the end of the molecule, α-olefins can form adducts with urea, if the remainder of the chain is not branched. This urea reaction provided a means of obtaining enriched samples of α-olefins. The starting material was a 200° to 300° C. cut of hexane-solubles obtained by the solvent extraction of primary tar. Table V shows the composition of the α-olefins concentrate and of the oil which failed to adduct with urea. Therefore, α-olefin concentration of 17 to 18% was raised by this process to 50% as determined by infrared absorption.

The concentration of α-olefins was increased further by the use of silica gel separation to eliminate the paraffins and aromatics. A water-white fraction was obtained which contained about 75% α-olefins. Some trans and tertiary olefins were also present.

The individual small fractions obtained from the silica gel separation of the olefins from the whole adducted oil were subjected to further study. Table VI shows the information gained for representative olefin cuts about average molecular weight, ratio of α-olefins to total olefins, and total double bonds per molecule as determined by infrared and by bromine number. The average length of the olefin chains ranged from 14 to 16 carbon atoms, with most of the fractions containing about one double bond per molecule. The olefin fractions of highest molecular weight contained somewhat less unsaturation, which was probably evidence of incomplete separation of paraffins from the olefins. The olefin fractions of lowest molecular weight contained somewhat more than one double bond per molecule. No infrared evidence was found of conjugated unsaturation, which might be interpreted to suggest the presence of diolefins in which both double bonds are located terminally.

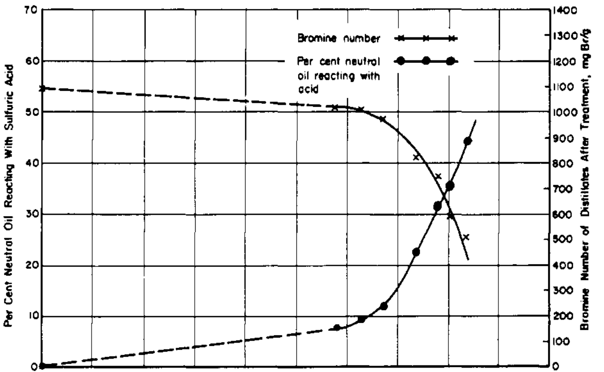

Figure 4. Effect of various strengths of sulfuric acid on neutral oil

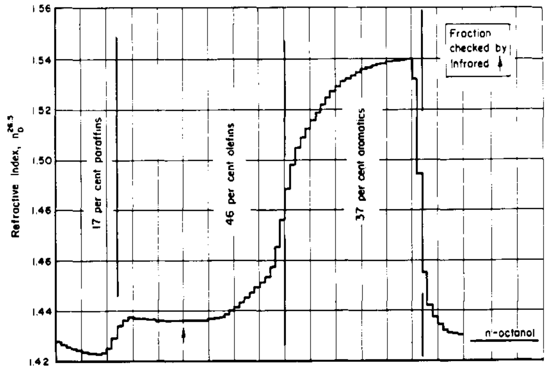

Figure 5. Silica gel adsorptogram for neutral oil washed with 78% sulfuric acid

Table IV. Composition of Neutral Oil before and after Being Washed with 78% H_2SO_4

	Neutral Oil Components[a], %			
	Paraffins	Olefins	Aromatics	Total
Original neutral oil	12	40	48	100
Washed neutral oil	11.6	31.3	25.2	68.1
Amount removed	0.4	8.7	22.8	31.9
Composition of removed material	1+	27+	71+	...

[a] Determined by displacement silica gel chromatography.

Table V. Composition of Products from Urea Adduction of 200° to 300° C. Cut of Hexane-Solubles

	Composition, %				
		Olefins			
Product	Paraffins	Alpha	Total	Aromatics	Yield from Charge Material
Adducted oil[a]	21	50	67	4	20
Nonadducted oil	12	..	23	65	80

[a] Contained 8% as intermediate fractions.

Table VI. Characterization of Olefin Cuts from Silica-Gel Chromatography of Oil from Urea Adduct of Distillate of Hexane Solubles

				Total Double Bonds/Mole	
Fraction[a]	Refractive Index, n_D^{20}	Molecular Weight[b]	Ratio of α-Olefins to Total Olefins[c]	By infrared	By bromination[d]
7	1.4385	233	0.74	0.6	..
8	1.4389	...	...	..	0.7
10	1.4386	225	0.78	0.8	..
11	1.4386	...	...	..	0.8
13	1.4387	215	0.77	0.9	..
14	1.4390	...	...	..	0.9
16	1.4393	209	0.77	1.0	..
17	1.4396	...	...	..	1.0
19	1.4399	206	0.77	1.0	..
20	1.4401	...	...	..	1.1
21	1.4412	...	0.75	1.1	1.2
22	1.4458	198	0.75	1.3	..

[a] Fractions 1 to 6 included paraffins and intermediate; fractions 23 to 24 included intermediate and aromatics.

[b] Determined cryoscopically in benzene.

[c] Determined by infrared spectroscopy. Olefins other than α-olefins remained about 75% trans and 25% tertiary from fraction to fraction.

[d] Br-BrO_3 method, ASTM D 1158-55T. Values under 1 probably indicate paraffin contamination; values over 1 may indicate a small amount of multiple unsaturation.

No work was done to prove the presence or absence of cyclic olefins in neutral oil, although such compounds are expected to be present. A ring analysis was made of the combined paraffin-olefin fraction (61% olefins), as separated by silica gel, of a 200° to 300° C. cut. Various physical measurements were used as recommended by Deanesley and Carleton (*2*) to calculate the results, which indicated about one fourth of the carbon atoms were naphthenic.

Aromatics. A concentrate of aromatics was obtained from neutral oil by the use of butyrolactone as selective solvent. The aromatic fraction was further purified by using silica gel and sodium amide in attempts to remove nonaromatics and particularly the polar compounds. The material was carefully rectified at reduced pressures into 45 fractions over a calculated atmospheric boiling point range of 140° to 290° C. Table VII summarizes the types of hydrocarbons definitely identified by infrared analysis of the individual fractions. Polar compounds were evident in the higher boiling fractions. Benzofuran and 2-methylbenzofuran were tentatively identified as major nonhydrocarbon contaminants.

Ring analysis of the aromatic concentrate based on physical properties showed the average structure to correspond to methyl or ethyl Tetralin. However, this conclusion may be in error because of polar contaminants. Even though special effort had been made to remove nonhydrocarbon contaminants, elemental analysis showed the concentrate to contain sulfur, nitrogen, and oxygen (by difference) as follows:

Hetero Atom	Elemental Percentage in Concentrate
S	2.4
N	0.2
O	1.6

There was no evidence of any significant amount of polynuclear aromatics or long-chain alkylaromatics.

Polar Compounds. A number of separation methods were applied to neutral oil in attempts to obtain polar compounds free of hydrocarbons. The only successful method involved use of silica gel with elution chromatography. Although other information suggests that neutral oil contains about 20% of polar compounds, only 12.5% was isolated by this particular method.

The polar fraction contained a small amount of aliphatic carboxylic acids as evidenced by a bicarbonate wash and infrared inspection of the regenerated acids. The nonacidic fraction was separated further by use of Girard's T reagent. Figure 6 shows the flow diagram for the separation and study of polar compounds in neutral oil.

Infrared examination of the ketone fraction showed it to be primarily aliphatic with a large amount of branching. The volatile portion of the fraction not reacting with the Girard reagent showed infrared evidence of hydroxyl, imino, and cyano groups as well as carbonyl.

Sulfur-containing compounds are also present in polar compounds, but spectral evidence is not satisfactory for identification of most classes of sulfur compounds. Furthermore, although chromatography is often effective for the separation of sulfur compounds from hydrocarbons, the sulfur compounds in lignite tar could not be cleanly separated by this technique. The sulfur compounds in lignite tar are chemically unreactive. Reactive compounds such as thiols and disulfides appear to be present, but in relatively low concentration as compared with aliphatic and cyclic sulfides. Thiophenes were not believed to be present; because they are relatively strong infrared absorbers, any significant amounts would have been detected.

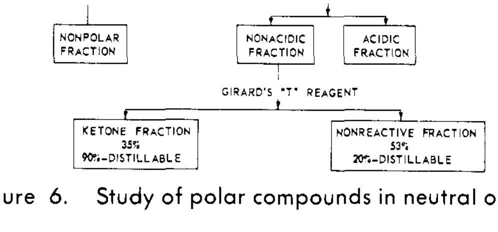

Figure 6. Study of polar compounds in neutral oil

Table VII. Summary of Hydrocarbon Types Found by Infrared Spectroscopy in Fraction of Refined Aromatic Concentate

Boiling Range, ° C. / 1 Atm.	Characterization
140–163	Principally xylenes
157–182	C_9 aromatics, principally trimethylbenzenes
176–205	C_9 and higher aromatics including indene and hydrindene
202–231	Naphthalene plus other aromatics
223–252	Methylnaphthalenes
248–291	Possibly dimethylnapthalenes plus other aromatics

Table VIII. Summary of Chemical Classes in Texas Lignite Tar

Tar acids, 26%	Low-boiling	5%	Phenols, cresols, xylenols, ethylphenols
	High-boiling	21%	Phenols, napthols, indanols, polyhydroxylic phenols
Neutral oil, 70%			
	Paraffins	10%	Straight-chain, lightly branched
	Olefins	25%	Alpha, trans-internal, tertiary
	Aromatics	21%	Benzenes, naphthalenes, hydrindenes, indenes
	Polar compounds	14%	Ketones, sulfides, nitriles
Tar bases, 4%	Heterocyclics	4%	Pyridines, quinolines

The make-up of the tar by classes of chemicals is summarized in Table VIII. Considerably more effort will be needed to obtain more detailed data. This is particularly true for the constituents in the high-boiling fractions of the tar. In any of the classes of chemicals, a large number of individual chemical compounds are present.

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