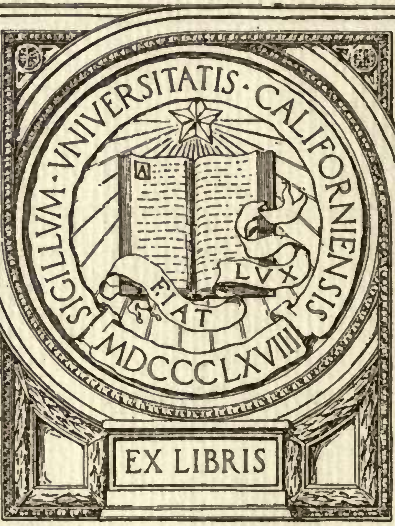

Examination of Low-Temperature Coal Tar

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science
Columbia University, in the
City of New York

n.e.
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By
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New York City
1922

Acknowledgments

The author takes pleasure in acknowledging the kindly co-operation of Prof. J. J. Morgan, at whose suggestion the present investigation was undertaken, and the many courtesies of Dr. H. A. Curtis of the Clinchfield Carbocoal Corporation.

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Examination of Low-Temperature Coal Tar

I. Characteristics of Low-Temperature Tar

Outline of a Scheme of Examination for Tars Obtained in the Low-Temperature Carbonization of Coal—Composition of a Commercial Low-Temperature Tar and Comparison With Coke-Oven and Gas-Works Tars—Review of Results Obtained by Previous Investigators

BY ROLAND P. SOULE

THE present report is the first of a projected series of studies in the carbonization of coal. It concerns itself primarily with an examination of a low-temperature coal tar, but its scope has not been confined to specific analytical data. In the absence of any standard analytical procedure in this little explored field, it has become necessary to develop a scheme of examination by which the component groups of low-temperature tars may be readily examined. An intensive investigation has been made of a commercial low-temperature tar, comparing the analytical results obtained with those of other tars. This scheme and the character of the tar determined by it are described in the present paper.

The composition of this tar indicates a stage in the decomposition of the primary liquid distillates of coal which hitherto has not been carefully studied. In a second installment it is intended to define more precisely several distillation reactions, and to present a new viewpoint on the much disputed mechanism of the carbonization of coal. Thus, a rational basis will be found for reconciling to a large extent the reported differences in the composition of low-temperature coal tars.

Until recently the commercial carbonization of coal has been performed at 1,000 to 1,300 deg. C. primarily for the production of city gas and metallurgical coke. Within the past decade, however, lower temperatures of distillation have been made to serve two purposes. The first of these is scientific in nature—the study of the products of distillation at various temperatures has shed light on the constitution of coal, and afforded

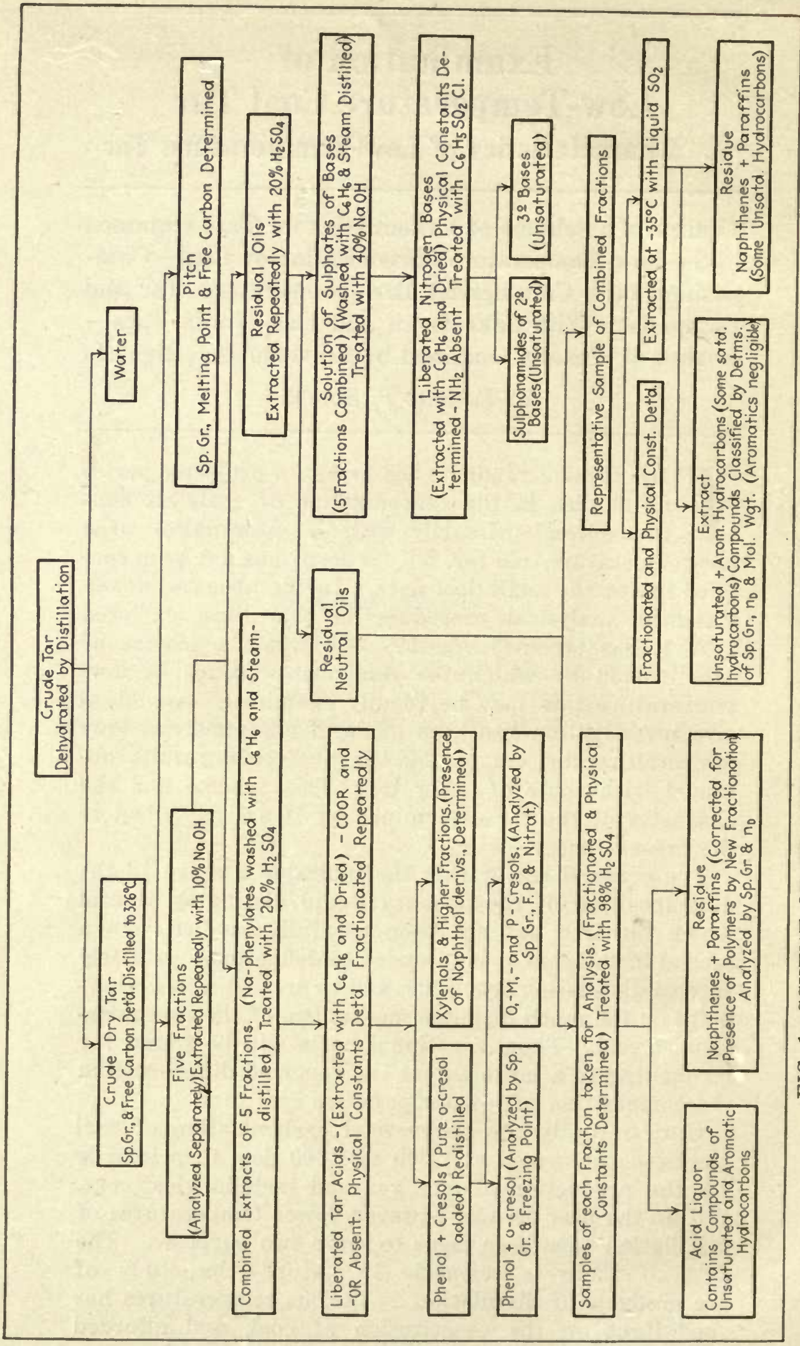

FIG. 1—SCHEME OF EXAMINATION OF A LOW-TEMPERATURE COAL TAR

evidence for theories of carbonization. The second object has been the production of new materials of commercial value. By distilling an ordinary bituminous coal at 500 to 600 deg. C. there are obtained a friable, free-burning coke which may be made to serve as a smokeless fuel, and a distillate which upon removal of the phenols resembles crude petroleum in properties and uses.

OUTLINE OF INVESTIGATION

An outline of the type of methods used in the present investigation is given in Fig. 1. According to this procedure the tar examined was found to have the composition indicated in general by Table I and Fig. 2.

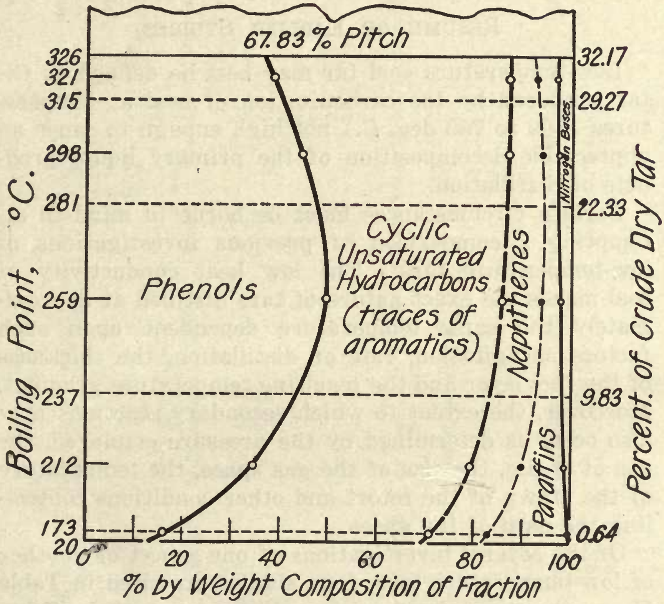

FIG. 2—COMPOSITION OF THE CARBOCOAL DISTILLATE

Fig. 2 shows the change in the percentages by weight of the various classes of components in the condensate as the boiling point of the tar rises during distillation. The vertical axis of boiling temperatures is so graduated that the areas of the figure represent proportions by weight of the different groups. The horizontal dotted lines separate the five fractions of the distillate, and the curved lines are the boundaries between the component groups.

TABLE I—SUMMARIZED COMPOSITION OF CARBOCOAL DISTILLATE

Component Classes	Percentages by Weight					
	Basis of Distillate			Basis Crude, Dry Tar		
Phenols	42.7			13.7		
Nitrogen bases	1.94			0.624		
Hydrocarbons	55.4			17.8		
Cyclic unsaturated (*a*)		41.5			13.4	
Saturated		13.9			4.4	
Naphthene			8.8			2.8
Paraffine			5.1			1.6
Totals	100.0	55.4	13.9	32.1	17.8	4.4

a May contain traces of aromatic hydrocarbons.

RÉSUMÉ OF EARLIER STUDIES

Low-temperature coal tar may best be defined as the tar produced by the carbonization of coal at temperatures (500 to 750 deg. C.) not high enough to cause an appreciable decomposition of the primary liquid products of distillation.

Certain circumstances must be borne in mind in attempting a comparison of previous investigations of low-temperature tars. The low heat conductivity of coal makes the exact nature of tars distilled at approximately the same temperature dependent upon such factors as agitation, rate of distillation, the thickness of the fuel layer and the resulting temperature gradient. Moreover, the extent to which secondary reactions may also occur is determined by the pressure employed, the use of steam, the size of the gas space, the temperature of the crown of the retort and other conditions controlling the path of the gases.

Of the several investigations of one aspect or another of low-temperature tars, four studies are cited in Table II as the most important and representative efforts toward a through analysis. A. Pictet[1] and his co-workers in Switzerland and D. T. Jones and R. V. Wheeler[2] in England employed the tar as an agent in their researches on the constitution of coal. S. W. Parr[3] and his associates in this country were primarily interested

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[1] A. Pictet et al., *Ann. Chim.* [9], vol. 10, p. 249 (1918) ; *cf.* A. Pictet and M. Bouvier, *Ber.*, vol. 46, p. 3342 (1913) ; vol. 48, p. 926 (1915) ; *Compt. rend.*, vol. 157, pp. 779, 1436 (1913) ; vol. 160, p. 629 (1915) ; A. Pictet, O. Kaiser and A. Labouchere, *Compt. rend.*, vol. 165, pp. 113, 358 (1917).

[2] D. T. Jones and R. V. Wheeler, *J. Chem. Soc.*, vol. 105, p. 140 (1914).

[3] S. W. Parr and H. L. Olin, Univ. Illinois Eng. Exp. Sta. Bulls. 60 (1912) and 79 (1915) ; T. E. Layng, Dissertation, Univ. Illinois (1915).

TABLE II—COMPARISON OF INVESTIGATIONS OF LOW-TEMPERATURE TARS

Name of investigators	Morgan and Soule		A. Pictet	Jones and Wheeler		S. W. Parr	F. Fischer
Date of investigations	1921—1922		1913—1918	1914—1915		1914—1915	1916—1919
Temp. of distn., deg. C.	500–600		450 max.	430		450–525	350–500
Distillation apparatus:							
Form	horizontal cylinder with rotating screws		2 horizontal D-shaped retorts, one above other	round-bottom flask		vertical cylinder	horizontal rotating cylinder
Material	Carborundum		Cast-iron	Jena glass		Cast-iron	Cast-iron
Dimensions	18 ft. x 7 ft.		....	about 1 liter		44 in. x 6 in.	110 cm. x 30 cm.
Amount distilled	5,000 lb.		1,500 kg	1.25 kg		20 lb.	10 kg.
Method	Dry		Dry	Dry		Superheated Steam	Steam
Pressure	atm.		15-20 mm. of Hg	13-15 mm. of Hg		<8 in. water above atm.	atm.
Time	3 hours		5 hours	5 weeks		6-8 hours	1-2 hours
Coal	Pa. "Pittsburgh Terminal"		Montrambert (Loire)	Scotch	Durham	Illinois (Vermilion Co.)	Lohberg gas coal
Analysis (dry basis), in per cent:							
Vol. comb. matter	35.30		15–20	20.36	30.81	34.92	39
Fixed carbon	57.92		66–75	70.36	65.09	48.81	59
Ash	6.78		10–15	3.28	4.10	16.27	1.65
Carbon	.....		.....	86.92	86.88	.....	80.68
Hydrogen	.....		.....	4.98	5.41	.....	5.54
Oxygen	.....		.....	5.56	4.71	.....	7.67
Nitrogen	1.65		.....	1.75	1.75	.....	1.90
Sulphur	1.77		.....	0.79	1.25	2.01	0.67
Crude, dry tar							
Per cent by weight of coal	11.3		4.0	6.5		8.7	10
Specific gravity	1.0676 at 15.5 deg./15.5 deg. C.		<1 fresh, 1 in 3 hr. >1 later	0.999 at 15 deg./15 deg. C.		1.072 at 15 deg. C.	"about 1"
Free carbon, per cent	0.71		.....	....		1.35	.....
Max. temp. distn. tar	326		steam distillation	300		400	superheated steam distn.
Pitch							
Per cent of tar	67.83		.....	50		30	.....
Melting point, deg. C.	53		.....	"soft"		110	.....
Specific gravity	1.134 at 15.5 deg./15.5 deg. C.		.....	1.128 at 15 deg./15 deg. C.		1.27	.....
Free carbon, per cent	2.17		.....	0		12	.....
Composition of tar, in per cent	Distillate	Tar	Crude, dry tar basis	Distillate	Tar	Crude, dry tar	Crude Tar
Phenols	42.7	13.7	(8[a])	12–15	6– 8	28.0	Phenols................50
Bases	1.94	0.624	0.2	traces	traces	0.2	Non-viscous oils........15
Alcohols	0.0	0.0	2	.....	.....	....	Lubricating oils.........10
Hydrocarbons							Paraffine................1
Paraffine	5.1	1.6	...				Resins..................1
Naphthene	8.8	2.8	30	40	20	14.5	Pitch...................6
Unsaturated	41.5	13.4	68	40–45	20–23		Loss and water.........17
Aromatic	....	....	0	7	3.5	57.3	

[a] Eight per cent of phenols found by Pictet in a later analysis.

in the commercial aspects of low-temperature carbonization, as were F. Fischer[4] and his staff in the Kaiser-Wilhelm Institute of Coal Research in Mülheim-Ruhr, Germany. The details tabulated in the case of Fischer's work represent only one of a large number of related experiments, but serve to indicate his characteristic method of reporting tar investigations in technical rather than in scientific terms. For the purpose of comparison the results obtained in the present investigation are also included in this table.

ORIGIN OF THE TAR EXAMINED

The tar examined was produced by the "Carbocoal" process[5] (C. H. Smith patents) of the International Coal Products Corporation. It was a representative sample made in March, 1921, under commercial conditions at the experimental plant of the company at Irvington, N. J.

The low-temperature tar produced by the *primary* retorts is the subject of this investigation. These retorts are horizontal, about 18 ft. long, and of cardioid section. The walls are constructed of carborundum blocks, and the ends of cast iron lined with firebrick. The coal is continuously stirred and advanced through the retort by paddles of radius 2 ft. 3 in. mounted on two parallel 12-in. paddle shafts, which revolve at 1.8 r.p.m. Each retort is operated about one-third full, and has sufficient capacity to permit an output of 1 ton an hour. The products of distillation leave at the top of the discharge end of the retort. The temperature in the retort shell is about 730 deg. C., in the gas at the feed end of the retort 300 deg. C. and at the discharge end about 500 deg. C. The temperature of the discharged coke approximates 480 deg. C.

It is apparent from this description of retort conditions that the opportunities for secondary decomposition are not negligible. Thus the outgoing products of distillation come into contact with surfaces heated to 600 deg. C. and undergo decomposition to some extent.

A Pennsylvania bituminous coal known as "Pittsburgh Terminal" coal was used in the preparation of the

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[4] F. Fischer and W. Gluud, *Ges. Abhandl. zur Kenntnis der Kohle*, vol. 1, p. 114 (1916); *Ber.*, vol. 52, p. 1035 (1919): *cf.* also *Ges. Abhandl.*, vol. 3, pp. 1, 248, 270 (1918).

[5] H. A. Curtis, CHEM. & MET. ENG., vol. 23, p. 499 (1920); *J. Ind. Eng. Chem.*, vol. 13, p. 23 (1921); G. H. Thurston, *J. Soc. Chem. Ind.*, vol. 40, p. 51T (1921); Wallace Savage, CHEM. & MET. ENG., vol. 19, p. 579 (1918); C. T. Malcolmson, *Bull. Am. Inst. Min. Eng.*, vol. 137, pp. 971, 1686 (1918).

sample of tar examined. Its analysis[6] on a dry basis is given in Table II. The moisture content of the coal as fed into the furnace amounted to 2 per cent. The calorific value was 13,925 B.t.u. per lb.

PROPERTIES OF THE TAR AND PITCH

Dehydration and Distillation. Carbocoal tar, in common with other low-temperature tars, is a black oil of petroleum-like fluidity. It smells strongly of cresols and to a less extent of hydrogen sulphide. The viscosity is lower than that of ordinary coke-oven and gas-works tar, and no odor of ammonia or naphthalene can be detected in it.

The tar was dehydrated for subsequent examination by distilling to 200 deg., separating the light oil from the water in the condensate and returning it to the main body of tar remaining in the still. A specially constructed 3-gal. copper tar-still of the same proportions as the Barrett type[7] was used in the operation. About 8 kg. of tar was distilled at a time. The content of water in the sample of tar amounted to 2.12 per cent.

A sample of thoroughly mixed, crude, dry tar was taken for specific gravity (Hubbard bottle) and "free carbon" determinations according to standard procedures[7]. A dry distillation of the 8 kg. of crude tar thus dehydrated was made at atmospheric pressure in the same copper still. The rate was 15 c.c. per minute, or about 0.2 per cent of the total volume of tar per minute. For comparison samples of coke-oven tar[8] and gas-works tar[9] were fractionated in exactly the same manner and the results are recorded in Fig. 3 and Table III.

In general there is a close resemblance between the three fractionation curves, disproving the many exaggerated statements that have been made of the larger quantity of low-volatile oils in low-temperature coal tars. The percentage of pitch is only slightly lower in this tar than in the high-temperature tars, although the difference would be greater with higher cutting temperatures, or if the distillates had been carried to

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[6] Analysis by Research Laboratory of the International Coal Products Corporation.

[7] J. M. Weiss, *J. Ind. Eng. Chem.*, vol. 10, pp. 732, 817 (1918).

[8] Obtained through the courtesy of the Seaboard By-Products Coke Co., Kearny, N. J. (Koppers retorts); distilled at 850-900 deg. from a mixed coal, avg, 30 per cent V.C.M.

[9] Obtained through the courtesy of the Consolidated Gas Co., New York City; consists of approximately equal proportions of horizontal and inclined retort tars; coal distilled at about 1,000 deg.

TABLE III—FRACTIONATIONS OF REPRESENTATIVE TARS[10]

Fraction B.P. Range Deg. C.	Percentages of Total Weight Low-Temperature Tar	Coke-Oven Tar	Gas-Works Tar
20–173	0.64	0.70	1.19
173–237	9.19	8.27	9.22
237–281	12.50	12.44	10.12
281–315	6.94	6.21	3.78
315–326	2.90	2.53	1.93
Pitch (diff.)	67.83	69.85	73.76
M. P. of pitch, Deg. C.	53	69	89

a pitch of the same melting point in each case, as commercial conditions might demand. Thus, when Carbocoal tar is carried to a pitch melting at 80 deg. C. for use in briquetting, only 56 per cent remains in the still.

Pitch. The pitch obtained from the low-temperature tar was an amorphous, black residue, which lacked the brittleness and lustrous fracture of high-temperature pitches. Briquets made from it lost their sharp edges

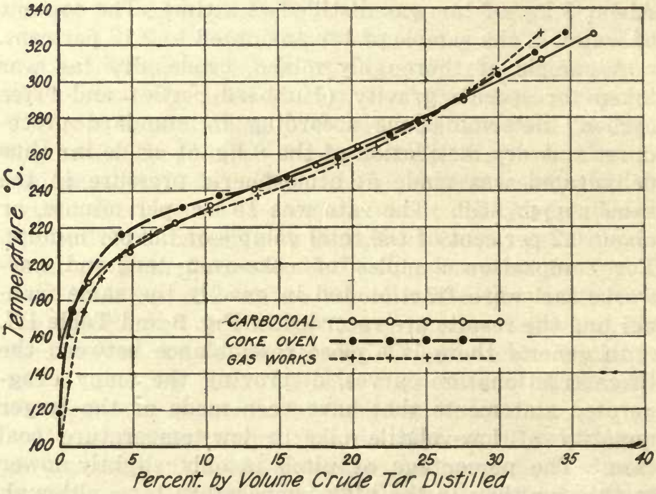

FIG. 3—DISTILLATION OF CRUDE, DRY TARS

TABLE IV—COMPARISON OF TARS AND PITCHES

	Low-Temperature	Coke-Oven	Gas-Works
ude, dry tar			
Sp.gr. 15.5 deg./15.5 deg.	1.0676	1.1845	1.2172
"Free carbon," per cent	0.71	6.93	20.1
Pitch, cut at 326 deg.			
Sp.gr. 15.5 deg./15.5 deg.	1.134	1.263	1.312
"Free carbon," per cent	2.17	16.8	31.1
Air melting point, deg. C.	53	69	89

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[10] All temperatures reported in this investigation are corrected for the emergent stems of the thermometers.

within an hour at room temperature. The specific gravity (Hubbard bottle), "free carbon" and air melting points of the Carbocoal, coke-oven and gas-works tars and pitches were determined by standard procedures, and are recorded in Table IV.

The Phenols

The high content of phenols in low-temperature tars has been remarked by nearly all investigators (*cf.* Table II), and within certain limits may be accepted as an important characteristic distinguishing them from high-temperature tars.

Removal From the Tar. The percentages of phenols were determined separately in each of the five fractions (*cf.* Table III). In the method used, 100 g. of a fraction was weighed into a 200-c.c. glass-stoppered separatory funnel, and extracted four times each with 50 c.c. of 10 per cent sodium hydroxide solution. The loss in weight of each sample checked against the gain in weight of the alkali used was taken as the percentage of tar-acids present.

Fig. 4 was obtained by plotting percentages of tar-acids against the average boiling points during distillation of the corresponding tar fractions, taken as the mean ordinates of the respective sections of the distilla-

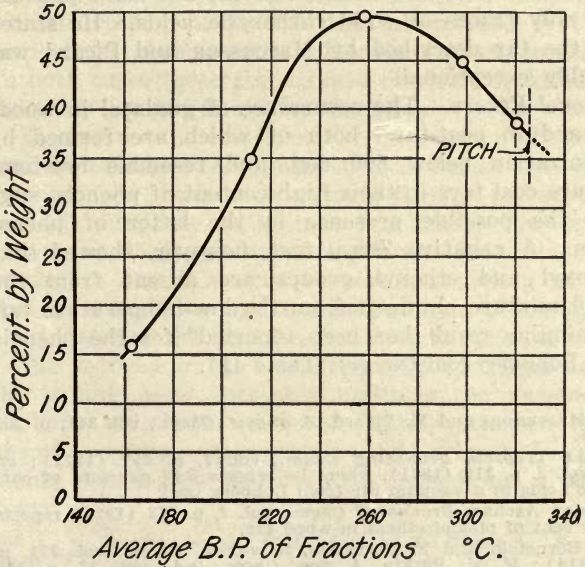

FIG. 4—RELATION OF THE BOILING POINTS OF TAR FRACTIONS TO PHENOL CONTENT OF EACH

tion curve of Fig. 3. It shows a well-defined maximum between 240 and 280 deg., and indicates that a large quantity of tar acids is contained in the pitch.

Purification of the Tar-Acids. The fractions of low-temperature tar were washed completely free of phenols with 10 per cent sodium hydroxide solution. The alkaline solution, after purification by benzene extraction and steam distillation, was acidified with 20 per cent sulphuric acid to liberate the phenols, as indicated by Fig. 1. The tar-acids thus recovered formed a dark brown, slightly viscous liquid, which had a strong odor of cresols.

Carboxylic Acids. No solubility of this mixture in a saturated sodium carbonate solution could be detected, and a sample after solution in sodium hydroxide was completely recovered by precipitation with carbon dioxide. Carboxylic acids, therefore, could be admixed with the phenols only to a negligible extent.

None of the four investigators quoted above has reported such compounds, but recently Marcusson and Picard[11] found in a low-temperature tar from upper Silesian coal a solid mixture of 13 per cent phenols and 12 per cent aromatic carboxylic acids. Tropsch[12] distilled under similar conditions a coal from the same region, however, and found viscous, not solid phenols, with only traces of solid carboxylic acids. He stated that the tar described by Marcusson and Picard was probably exceptional.

Phenol Ethers.—The occurrence of guaiacol in wood-tar[13] and in peat-tar,[14] both of which are formed by carbonization below 500 deg. and resemble low-temperature coal tars in their high content of phenols, suggests the possible presence in the latter of phenol ethers. A negative Zeisel test, however, showed that methoxyl and ethoxyl groups are absent from the phenol mixture obtained from the low-temperature tar.

A similar result has been reported[15] for the phenols from Lohberg coal tar (*cf.* Table II).

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[11] J. Marcusson and M. Picard. *Z. angew. Chem.*, vol. 341, p. 201 (1921).

[12] Hans Tropsch, *Brennstoff Chem.*, vol. 2, p. 251 (1921); *cf. ibid.*, vol. 2, p. 312 (1921), where he reports 0.49 per cent of carboxylic acids in a vacuum tar from Lohberg coal.

[13] Ossian Aschan, *Brennstoff Chem.*, vol. 2, p. 273 (1921) reports 4.9 per cent of phenol ethers in wood tar.

[14] E. Börnstein and F. Bernstein, *Z. angew. Chem.*, vol. 271, p. 71 (1914); F. M. Perkin, *J. Soc. Chem. Ind.*, vol. 33, p. 395 (1914); *J. Inst. Pet. Tech.*, vol. 1, p. 76 (1914).

[15] W. Gluud and P. K. Breuer, *Ges. Abhandl.*, vol. 2, p. 236 (1917).

Polyhydroxy Phenols. The water obtained simultaneously with the tar in the distillation of the coal in the low-temperature process was not available for the present investigation. Since this liquor contained the largest proportion of polyhydroxy phenols distilled from the coal, their estimation in the tar was not attempted.

Catechol has been identified[16] among the products of low-temperature distillation of Lohberg coal, and was estimated to be present to the extent of 0.02 per cent of the weight of the coal.

FRACTIONATION AND DENSITY DETERMINATIONS

The phenol mixture from the low-temperature tar had a specific gravity[17] of 1.036 at 25 deg./4 deg. as compared with 1.044 of the mixed coke-oven and gas-works phenols extracted with 10 per cent sodium hydroxide at 60 deg., and purified in the same manner as the low-temperature phenols. Fractionation curves of the two types are seen in Fig. 5.

It is evident that in the first-named mixture there are no phenols of boiling point higher than may be found among the high-temperature phenols. The proportions of the components, however, differ quite markedly, 52 per cent by volume of the low-temperature phenols boiling below 220 deg., as opposed to 77 per cent of the phenols from coke-oven and gas-works tar. In both cases these percentages may be increased considerably by continued fractionation.

To obtain a more informative comparison of the low- and high-temperature phenols, each series was slowly distilled four times with a Young four-pear head, dividing the distillate into eight fractions. The specific gravity at 25 deg./4 deg. of each was determined, and plotted in Fig. 6 against the average boiling point of that fraction, taken as the mean ordinate of the boiling-point curve of the final fractionation in each case.

The decrease in the specific gravity of the phenols as the boiling point increases indicates the presence of aliphatic sidechains of lower density attached to the phenol nucleus—e.g., cresols and xylenols. In the higher homologs a sharp rise in density and a notable

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[16] W. Gluud, *Ges. Abhandl.*, vol. 3, p. 66 (1918); *cf.* W. Gluud and P. K. Breuer, *loc cit.* (ref. 15), and E. Börnstein, *Ber.*, vol. 35, p. 4324 (1902).

[17] Unless otherwise specified, all densities cited in this investigation were determined by use of a Becker analytical balance and a 7 g. glass plummet immersed in the liquid, which was jacketed with water at the desired temperature.

TABLE V—FRACTIONATION OF PHENOLS FROM LOW-TEMPERATURE TAR

No.	Fraction, Deg. C.	Weight in G., Fraction	Per Cent of Total Phenols	No.	Fraction, Deg. C.	Weight in G., Fraction	Per Cent of Total Phenols
1	182–189	41	7.3	6	214–220	44	7.9
2	189–195	38	6.8	7	220–227	14	2.5
3	195–202	60	10.8	8	227–260	102	18.3
4	202–207	71	12.7	9	260–300	92	16.5
5	207–214	48	8.6	10	Pitch	48	8.6
					Total	558	100.0

increase in the viscosity of the fractions mark the appearance of α- and β-naphthols[18] in the high-temperature phenols, and bicyclic compounds at least in the low-temperature phenols.

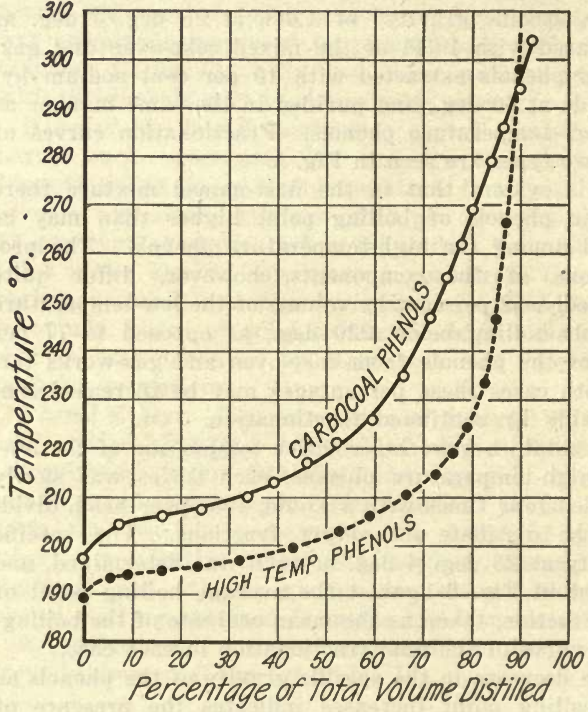

FIG. 5—DISTILLATION OF PHENOLS

These higher homologs have been investigated,[19] and found to contain naphthol derivatives, as the wide divergence of the two curves suggests, but neither α- nor β-naphthol. However, the coincidence of the

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[18] K. E. Schulze, *Lieb. Ann.*, vol. 227, p. 143 (1885).

[19] Unpublished investigation of M. T. Bogert and S. Caplan, to whom are due the data in Fig. 6 on the three highest-boiling fractions.

first section of the curves indicates that the Carbocoal mixture contains the same low-boiling components as the high-temperature phenols, although the proportion is much smaller.

Another sample of the mixed phenols was fractionated once each with a Young four-pear and a 10-in. Vigreux column, and then five additional times below 230 deg. with the Vigreux head. The average rate of distillation was 1 c.c. per minute, or 0.2 per cent by volume per minute. The results, corrected for the slight distillation losses, are recorded in Table V.

The specific gravity and bromine tests of Fraction 1 indicated the presence of phenol. Fraction 2 showed with ferric chloride the characteristic color reaction of *o*-cresol. In classifying these fractions it is customary to assume that if the cut is made midway between the boiling points of two components, the quantity of the higher-boiling compound appearing in the lower fraction will be approximately balanced by an equal amount of the lower-boiling compound in the higher fraction. Subsequent experiments have shown this assumption to be justified. On this basis Fractions 1 through 4 contain phenol and the cresols (210 g.; 37.6 per cent); Fractions 5 through 7 contain the xylenols (106 g.; 19.0 per cent); and Fractions 8 through 10 contain the higher homologs (194 g.; 34.8 per cent).

ESTIMATION OF PHENOL AND THE CRESOLS

The general scheme employed is that indicated in Fig. 1. The phenol and cresols, separated from the higher homologs by 15 fractionations, amounted to 35.0 per cent (uncorrected for distillation losses; *cf.* 37.6 per cent above) of the total phenols. Since *m*- and *p*-cresols preponderated in the mixture thus obtained, pure *o*-cresol was added to accomplish a sharper separa-

TABLE VI—COMPOSITION OF THE LOW-TEMPERATURE PHENOLS

	Percentages by Weight, Basis of		
Component	Phenols	Distillate	Crude Tar
Phenol	4.2	1.9	0.6
Cresols [a]	33.4	15.2	4.9
Xylenol fraction	19.0	8.7	2.8
Higher homologs	34.8	15.9	5.1
Pitch (acid resins)	8.6	3.9	1.3
Totals	100.0	45.6	14.7

[a] Ratio: 27 per cent ortho-, 19 per cent meta-, and 54 per cent para-cresols.

tion by distillation into two fractions, one comprising essentially phenol and *o*-cresol, and the other a mixture of the three cresols.

These fractions were analyzed separately by methods

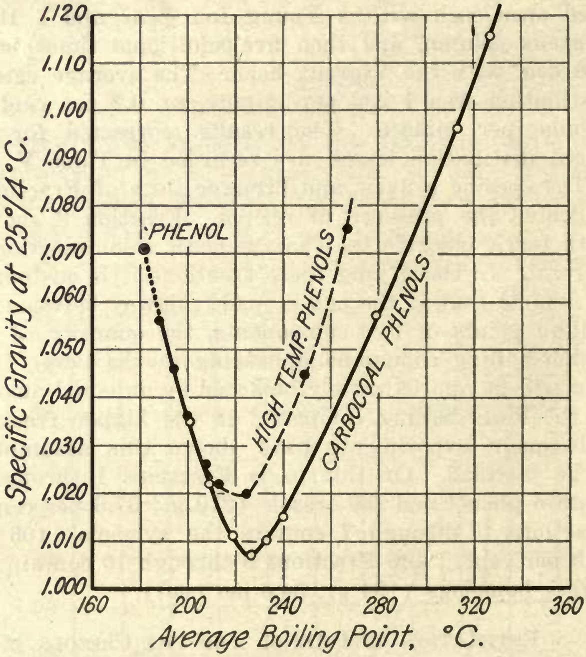

FIG. 6—BOILING POINT VS. SPECIFIC GRAVITY OF PHENOLS

involving nitration[20] and the determination of density and freezing points.[21] Table VI shows the composition of these phenols.

COMPARISON WITH PREVIOUS INVESTIGATIONS

The yield of tar in the Carbocoal process from the particular coal in question is 225 lb. per ton, or 11.3 per cent. This is higher than any other yield reported in Table II. The reason for this lies to a large extent in differences in the composition of the coal used by various investigators, as indicated by Table VII.

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[20] F. Raschig. *Z. angew. Chem.*, vol. 14, p. 759 (1900).

[21] J. J. Fox and M. F. Barker, *J. Soc. Chem. Ind.*, vol. 36, p. 842 (1917); vol. 37, 265T, 268T (1918); vol. 39, p. 169T (1920); H. M. Dawson and C. A. Mountford, *J. Chem. Soc.*, vol. 113, pp. 923, 935 (1918). J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, vol. 9, p. 569 (1917); G. W. Knight, C. T. Lincoln, G. Formanek and H. L. Follett, *ibid.*, vol. 10, p. 9 (1918).

TABLE VII—COMPARATIVE YIELDS OBTAINED IN VARIOUS INVESTIGATIONS

Investigation	Temp. of Distillation, Deg. C.	Time of Distillation	Per Cent V.C.M. in Coal	Tar Yield Per Cent Wgt., Coal	Per Cent Tar-Acid Dist.	Per Cent Tar-Acid Tar
Pictet	450 max.	5 hr.	15–20	4.0	....	8
Jones & Wheeler	430	5 wks.	26–31	6.5	12–15	6–8
Parr	450–525	6-8 hr.	35	8.7	40	28
Morgan & Soule	500–600	3 hr.	35	11.3	43	13
Fischer	350–500	1-2 hr.	39	10.0	..	50

For the purpose of comparison it may be noted in connection with this table that the distillation of a 30-35 per cent volatile coal in a coke oven at 900-1,000 deg. C. yields from 4 to 6 per cent of tar. The phenols recovered from the coke-oven and gas-works tar mentioned above averaged about 9 per cent by weight of the distillate, or 2.5 per cent of the total tar.

It must be borne in mind in studying these results that Pictet and Fischer alone actually removed the phenols from the entire tar, and that the percentages of tar-acids in the total tars reported by the others are consequently somewhat too low. As an added complication, Parr[3] reports a decrease in the yield of tar-acids with a decrease in the amount of steam used in the distillation of the coal. In general, however, it will be observed that the content of phenols increases with a rise in the volatile content of the coal from which it was distilled, and hence with the actual yield of tar. It seems apparent, therefore, that this increase in bulk of the tar is due largely to phenols.

The comparison of Table VII is superficial, however, and the underlying cause of this relationship is probably not so simple a matter as the mere volatile content. It has been shown[22] that the phenols owe their origin to the fraction of coal insoluble in pyridine and chloroform (the so-called "cellulosic" constituent), which is not a direct function of the volatile content. A low content of phenols in a tar, therefore, cannot be taken as direct evidence of a high temperature of coal carbonization unless the constitution of the coal distilled is also taken into consideration.

Previous Analyses of Low-Temperature Phenols

Jones and Wheeler[2] collected the fraction of phenols distilling between 100 and 145 deg. C. at 30 mm. (d.

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[22] D. T. Jones and R. V. Wheeler, *J. Chem. Soc.*, vol. 107, p. 1318 (1915); vol. 109, p. 707 (1916); *cf.* S. R. Illingworth, *J. Soc. Chem. Ind.*, vol. 39, p, 111T (1920).

1.037 at 15 deg./15 deg.), and from its ultimate analysis concluded it to consist essentially of a mixture of cresols and xylenols. Pictet[1] stated that the phenols obtained in fresh Montrambert "vacuum tar" have a very high boiling point, crystallize easily and contain no phenol, cresols or xylenols. Among the phenols which appeared on standing in a sample of tar prepared 5 years before, he was able to identify phenol itself, the three cresols and 1:2:4 xylenol by qualitative tests.

Fischer[23] reported the 45 per cent of phenols from Lohberg gas coal to contain 0.25 per cent catechol, 0.06 per cent phenol, 1 to 2 per cent cresols, 1 to 2 per cent xylenols, 30 to 32 per cent higher-boiling than xylenols, and 10 per cent acid resins. Phenol was determined by a freezing-point method[24] in a mixture obtained by fractional neutralization of the tar-acids. The cresols were studied by a development of Lederer's chloracetic-acid method[25] using Raschig's nitration method[20] as an alternative procedure for *m*-cresol. The amount of *m*-cresol was about one-quarter of the total cresols, which checks roughly the 19 per cent found in the cresols from low-temperature tar.

The Nitrogen Bases

Percentage of Bases. The percentages of bases in low-temperature tar were determined in four of the five phenol-free fractions of the tar distillate by a gravimetric method similar to that used for the tar-acids (*cf.* Fig. 1). Since the quantity of bases contained in the first fraction (20-173 deg.) was too small for quantitative extraction with 20 per cent sulphuric acid, however, recourse was taken to a titration method, using methyl orange as indicator.[26]

The results of these analyses are recorded in Fig. 7, where the percentages of bases in each tar-fraction are plotted against the average boiling point of that fraction during distillation. The rapid rise of this curve indicates that the pitch probably contains a greater quantity of these compounds than the distillate.

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[23] F. Fischer, *Brennstoff Chem.*, vol. 1, pp. 31, 47 (1920).

[24] Franz Fischer and P. K. Breuer, *Ges. Abhandl.*, vol. 3, p. 82 (1916); *cf. ibid.*, vol. 2, p. 236 (1917); F. Fischer and H. Gröppel, *Z. angew. Chem.*, vol. 301, p. 76 (1917); *Ges. Abhandl.*, vol. 2, p. 178 (1917).

[25] L. Lederer, *Frdl.*, vol. 4, p. 91 (1894/1897); D.R.P. 79,514.

[26] W. Gluud and P. K. Breuer, *Ges. Abhandl.*, vol. 3, p. 227 (1918).

Examination and Classifications. The crude tar-bases, recovered and purified as indicated in Fig. 1, formed a non-viscous, dark brown liquid mixture with a strong odor of pyridine. Having ascertained that the decomposition resulting was negligible, a sample was rapidly distilled to dryness to obtain a clear distillate for the later tests.

The bases showed a negative carbylamine reaction, and with nitrous acid evolved insufficient nitrogen to be measured. Primary bases could therefore be present only to a negligible extent. A saturated solution of sodium nitrite precipitated a mixture of nitrosamines from a hydrochloric acid solution of the bases. After purification their nature was verified by the Liebermann and diphenylamine reactions. The tests were both pronounced, and demonstrated the presence of secondary amines.

Hinsberg's benzene-sulphonyl-chloride method was used to separate the secondary from the tertiary bases. A precipitate of sulphonamides was formed,

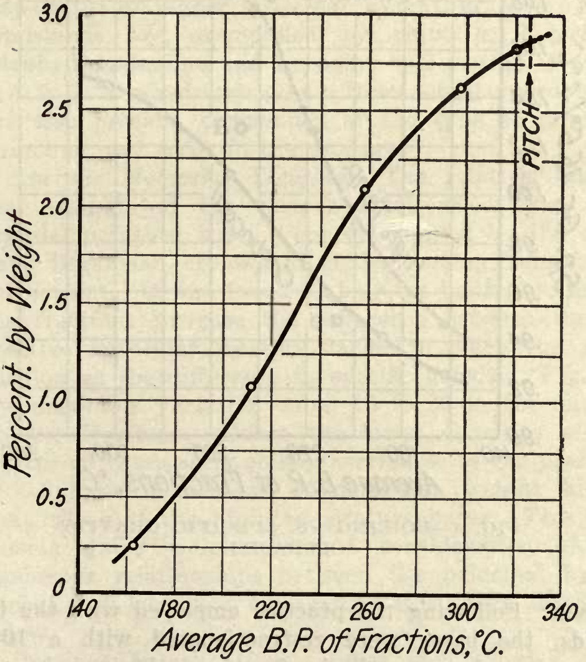

FIG. 7—RELATION OF BOILING POINT OF TAR FRACTIONS TO PERCENTAGE OF BASES CONTAINED IN EACH

which was completely insoluble in alkali. On acidification, 80 per cent of the sample passed into the acid layer. The Carbocoal bases, therefore, contained no primary, about 20 per cent secondary, and 80 per cent of tertiary bases. The purified tertiary bases recovered by this method and the sulphonamides prepared from the secondary bases rapidly reduced a 1 per cent aqueous solution of potassium permanganate, indicating unsaturation.

Fractionation and Specific-Gravity Determinations. The density of the mixture of low-temperature bases was 0.993, and that of the high-temperature bases was 1.060 at 15.5 deg./4 deg. C. Comparative fractional distillations showed that the bases from low-temperature tar are lacking in any preponderant single component analogous to quinoline in the high-temperature

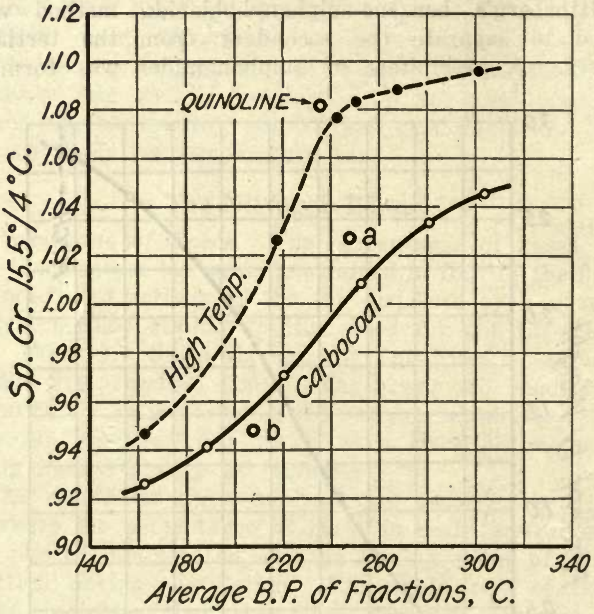

FIG. 8—BOILING VS. SPECIFIC GRAVITY OF BASES

bases. Following the practice employed with the tar-acids, the bases were re-fractionated with a 10-in. Vigreux column, and six fractions obtained in each case. The specific gravities of the fractions, determined after drying over solid potassium hydroxide, are plotted in Fig. 8 against the corresponding average boiling points (determined graphically). These curves demonstrate that the low-temperature bases are in general quite different in composition from those in ordinary coke-oven and gas-works tar. This is contrary to the case of the tar-acids (Fig. 6).

The smallest difference in density between the low- and high-temperature bases occurs in the low-boiling fractions. The first fraction of the low-temperature bases had a strong odor of pyridine, and was the only fraction appreciably soluble in water. With α-dinitrochlorbenzene it showed the characteristic red-violet color of the pyridine derivative. In common with ordinary tar, therefore, low-temperature tar contains some pyridine.

In the distillates between 230 and 260 deg. the densities of the bases are about 0.07 lower than those of the corresponding fractions of the quinoline-containing high-temperature bases. This difference indicates in the low-temperature bases a greater degree of hydrogenation of the nucleus, the presence of aliphatic side-chains of higher molecular weight, or both. Such compounds are exemplified by point *a*, N-methyl-tetrahydroquinoline and by point *b*, 2 methyl, 3 ethyl, 1:4:5:6 tetrahydropyridine. Since unsaturated bases are also present, compounds of the type of dihydroquinoline may occur in the mixture.

Average Molecular Weights. The relative[27] molecular weights of the various fractions of low- and high-temperature bases were determined by the ordinary Beckmann cryoscopic method, using benzene as the solvent. It was found that as the boiling points of the fractions increase the difference between the respective molecular weights varies in much the same fashion as the difference in specific gravity (Fig. 8), the maximum variation being 15 to 20 in the middle-boiling fractions. Hence the lower densities of the Carbocoal bases seem chiefly ascribable to the presence of aliphatic side-chains of molecular weight higher than those of the high-temperature bases. This conclusion gains weight from a consideration of the analogous relationships between the principal hydrocarbons of low- and high-temperature tars discussed below.

Previous Investigations. Jones and Wheeler[2] were

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[27] Pyridine bases are slightly associated in benzene solution.

unable to obtain more than traces of nitrogen bases in the small amount of tar at their disposal. Parr[3] reported an average of 0.23 per cent of "amines" on the basis of the crude, dry tar in the fractions boiling below 260 deg. C. Gluud[26] announced 0.46 per cent of "pyridine" in the Lohberg coal tar mentioned above (Table II). These investigators did not interest themselves in the nature of the bases.

Pictet[1] found 0.2 per cent of bases in the "vacuum tar" of Montrambert coal. He reported primary amines to be present, and identified the fraction 198-203 deg. as a mixture of toluidines. Pyridine and other tertiary amines appeared to be absent. Ultimate analysis of the picrates of the higher fractions showed them to be the dihydro-derivatives of quinoline and iso-quinoline. The significance of the absence of tertiary bases in this tar and their presence in low-temperature tar is discussed in the section on secondary carbonization reactions.

Alcohol and Sulphur Compounds

Alcohols. A sample of the low-temperature distillate freed of tar-acids and bases was boiled with metallic sodium, but no evolution of hydrogen or loss in weight of sodium was observed. Alcohols are therefore absent. Pictet[2] found 2 per cent of alcohols in "vacuum tar." The lowest-boiling component proved to be hexahydro-*p*-cresol; the others were isomers of monatomic phenols, a mixture of which they yielded on simple standing for a month. No other investigator has reported alcohols in low-temperature coal tars.

Sulphur Compounds. Hydrogen sulphide was determined (0.08-0.1 per cent) in the first two fractions of the low-temperature distillate, but most of this compound is to be found in the gaseous and aqueous products of distillation. A negative phenylhydrazine test showed the absence of carbon disulphide. Thiophene is indeterminate by the indophenine, thallin and mercuric salt tests in the presence of the large proportion of unsaturated hydrocarbons, which cannot be removed alone. No analyses of sulphur compounds are reported in the literature.

The Saturated Hydrocarbons

Examination of the Hydrocarbon Mixture. The neutral oils remaining after the extraction of the tar-acids and bases constitute the hydrocarbons of low-temperature tar. When freshly distilled, the lower fractions are pale yellow and the higher fractions amber colored. After standing for several weeks, all of the fractions become quite black in color, and deposit on the walls and bottoms of the bottles a thin, black coating. This is evidently due to the spontaneous polymerization or oxidation of a very small portion of the unsaturated compounds present, and is more marked in the lower than in the higher fractions. The density of fraction 20-173 deg. increased 0.012 on standing for 4 months.

The specific gravity of the total mixed hydrocarbons in the fresh distillate was found to be 0.891 at 25 deg./4 deg. as opposed to 1.028 of the coke-oven hydrocarbons distilled under similar conditions. Fractional distillation of the Carbocoal hydrocarbons shows the presence of no preponderant single compound such as the naphthalene of high-temperature tar. Since only a few very fine flakes of white crystals could be obtained in fractions cooled to —30 deg. C., only traces of solid aromatic hydrocarbons, such as naphthalene or anthracene, can be present in the low-temperature tar.

Composition of the Mixture: Separation of the Classes of Compounds. All fractions of the hydrocarbons from low-temperature tar instantly reduced a 1 per cent aqueous solution of potassium permanganate, and rapidly decolorized a solution of bromine in chloroform. Unsaturated hydrocarbons were therefore present in considerable quantity. Means for the qualitative detection of the other classes of components are lacking, however. Previous investigators have reported in low-temperature tars the following groups of hydrocarbons, listed in the order of their chemical activity:

1. Unsaturated (olefinic and cyclic).
2. Aromatic (liquid).
3. Naphthene (saturated cyclic).
4. Paraffine (liquid and solid).

Determination of the Percentage of Paraffine Plus Naphthene Hydrocarbons in the Neutral Residues. This analysis was accomplished by the treatment of 15 to 20 g. samples with 75 c.c. of 98 per cent sulphuric acid.[28] Each sample was agitated for half an hour in a glass-stoppered separatory funnel, and the weight of the residual oils determined. The results were cor-

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[28] H. G. Evans, *J. Soc. Chem. Ind.*, vol. 38, p. 402T (1919); F. B. Thole, *ibid.*, vol. 38, p. 39T (1919).

rected for polymerization[29] of the unsaturated hydrocarbons by a method based on redistillation of the residual saturated oils and subtraction of a quantity equivalent to the weight of the dissolved polymers. All determinations were made in duplicate, and the means of the closely agreeing values are plotted in Fig. 2. The percentage of saturated hydrocarbons thus obtained (13.9 per cent) is much lower than any previously reported (Table II). This is explained in the section on secondary carbonization reactions.

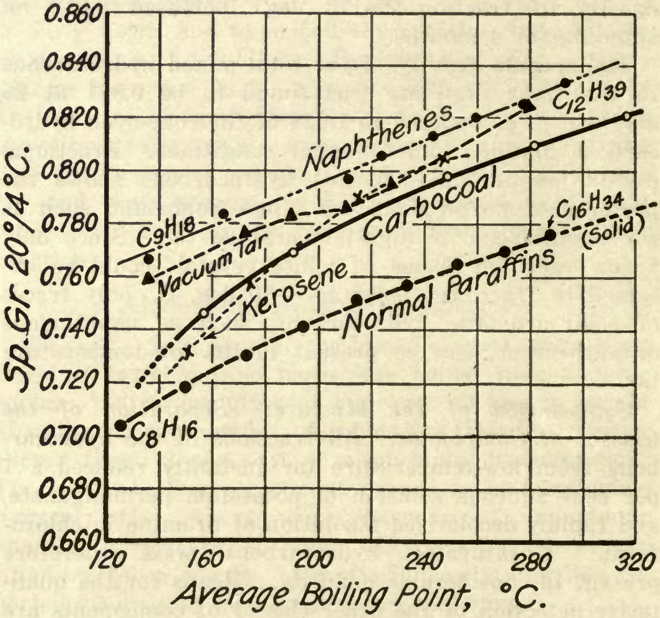

FIG. 9—SP.GR. OF SATURATED HYDROCARBONS

Estimation of the Naphthenes. The indices of refraction and specific gravities of the redistilled saturated hydrocarbons were determined. Fig. 9 shows that the graphical relation between the densities and boiling points of these residual oils offers a method of approximating the proportions of paraffines and naphthenes. The densities plotted for the naphthenes are those reported[30] for hydrocarbons of formula C_nH_{2n} isolated from crude petroleum. It is apparent that the position of the Carbocoal curve between the naphthene

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[29] B. T. Brooks and Irwin Humphrey, *J. Am. Chem Soc.*, vol. 40, p. 822 (1918).

and paraffine curves may be used as a basis of estimating the proportions of these groups of hydrocarbons. No great accuracy can be claimed for such an approximation, since the densities of the naphthenes vary slightly according to the nature of the hydrocarbon, although they are much less erratic than the corresponding indices of refraction. Representative values were selected, however, and it is believed that a fair picture may thus be obtained of the composition of the saturated hydrocarbons from low-temperature tar. The distillate thus contained 8.8 per cent naphthenes and 5.1 per cent paraffines.

An interesting sidelight on the nature of these hydrocarbons from low-temperature tars is given by a comparative examination of oils of the same boiling point from crude petroleum. A kerosene from the mid-continental field was washed thoroughly a number of times with oleum until no test was given for unsaturation. The water-white oil thus obtained after washing with alkali and redistilling possessed the same fragrant odor as the saturated hydrocarbons. The refractive indices and specific gravities (*cf.* Fig. 9) of the fractions of this refined kerosene reveal a striking similarity between these two groups of oils, one obtained from coal and the other from petroleum.

Previous Investigations. Previous investigators have interested themselves primarily in the qualitative study of individual compounds. Fischer and Gluud[31] cooled a dilute acetone solution of the oils to about —70 deg. C. with liquid air. They estimated that the "benzine" fraction (below 200 deg.), the "illuminating oil" fraction (200-300 deg.), and the "lubricating oil" fraction (above 300 deg.) each contained 10 per cent of paraffines. The paraffines boiling between 200 deg. and 300 deg. were liquid ($C_{10}H_{22}$ to $C_{19}H_{40}$) and those in the higher fractions were solid ($C_{24}H_{50}$ to $C_{29}H_{60}$).

Ultimate analysis has been employed by other investigators for the same purpose. Jones and Wheeler[2] reported a mixture of naphthenes with a small quantity of paraffines in the saturated fraction 35-125 deg. C. of their low-temperature tar, but concluded from the high percentages of carbon in the fractions boiling between 150 and 300 deg. that they "must consist of naphthenes only, or, what is less likely, of mixtures

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[30] C. F. Mabery, *Proc. Am. Acad, Arts and Sci.,* vol. 40, p. 323 (1914) ; Markownikoff and Ogloblin, *Berl. Ber.,* vol. 16, p. 1873 (1883) ; Konowaloff, *Chem. Z.,* vol. 14, p. 113 (1890).

[31] F. Fischer and W. Gluud, *Ges. Abhandl.,* vol. 2, p. 295 (1917) ; vol. 3, p. 39 (1918).

of paraffines with hydrocarbons richer in carbon than the polymethylenes." Solid paraffines ($C_{26}H_{54}$ and $C_{27}H_{56}$) were crystallized from the fraction 200-260 deg. at 30 mm.

Pictet[1] examined the six fractions of "vacuum tar" obtained between 135 and 285 deg. after extraction with liquid sulphur dioxide, and reported all to have the general formula of the naphthenes. He was able to identify the hexahydro-derivatives of mesitylene and durene. The only solid hydrocarbon found was a naphthene, melene ($C_{30}H_{60}$).

The Non-Saturated Hydrocarbons

The unsaturated and aromatic hydrocarbons constitute the second largest group in the low-temperature tar. The distillate contains 41.5 per cent of these compounds, while the tar-acids amount to 42.7 per cent. The low density and congealing point of the total hydrocarbon mixture point to the absence of ordinary

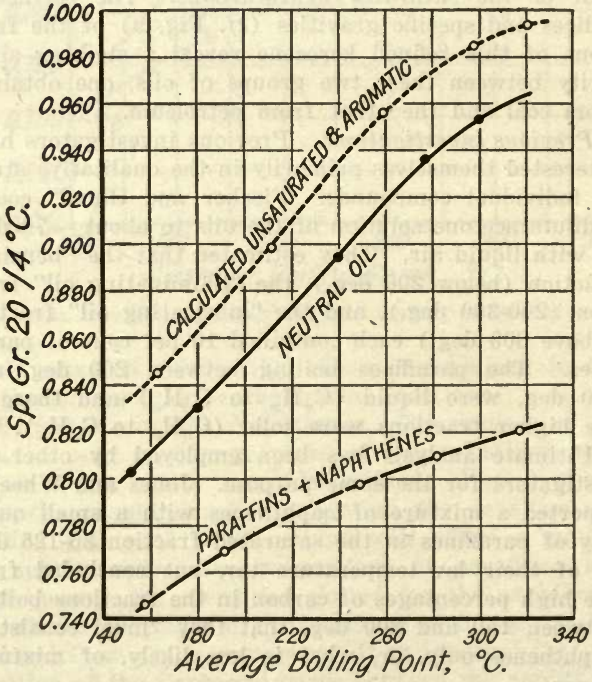

FIG. 10—SPECIFIC GRAVITIES OF HYDROCARBONS FROM LOW-TEMPERATURE TAR

solid aromatic hydrocarbons and to the preponderance of the unsaturated components. The specific gravities at 20 deg./4 deg. of the non-saturated fractions were calculated, as shown in Fig. 10, from the densities of the total neutral oils and of the saturated hydrocarbons, and from the known percentages of saturated hydrocarbons in the neutral oils. The curve thus obtained is too high for the densities of the olefines, and indicates that the unsaturated hydrocarbons are cyclic in character.

Recovery of the Non-Saturated Hydrocarbons. The only method that appears to offer a means of recovering the non-saturated (unsaturated and aromatic) hydrocarbons comparatively free from naphthenes and paraffines is extraction with liquid sulphur dioxide. Although the fraction 20-173 deg. is miscible with this solvent[32] in all proportions at —35 deg. C., the separations accomplished are sharper and more specific in hydrocarbon mixtures of high molecular weight. While non-saturated hydrocarbons can be recovered in this manner, doubt must be cast on their purity, therefore, because of the variation in the effect of the solvent throughout the wide range of compounds involved. In particular it is to be expected that the lower fractions will be found admixed with a portion of the naphthene and paraffine hydrocarbons.

Using a ratio of three parts by volume of oil to five parts of liquid sulphur dioxide and the apparatus and method described by Bowrey,[33] a hydrocarbon mixture constituting a representative sample of the combined fractions was resolved into two parts; an extract containing the non-saturated and a small quantity of low-boiling saturated hydrocarbons, and a residue composed principally of saturated hydrocarbons.

Examination of the Non-Saturated Hydrocarbons. The oils recovered from the sulphur dioxide layer were washed with alkali and subjected to three very slow fractionations with a Vigreux head. The distillates were water-white at first, but after exposure to the atmosphere for only a few minutes became amber colored; the higher fractions showed a violet fluorescence. All fractions could be distilled at atmospheric pressure with only slight decomposition. The specific

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[32] *Cf.* R. J. Moore, J. C. Morrell and G. Egloff, MET. & CHEM. ENG., vol. 18, p. 396 (1918).

[33] S. E. Bowrey, *J. Inst. Pet. Tech.*, vol. 3, p. 287 (1917) ; *Chem Trade J.*, vol. 60, p. 426 (1917).

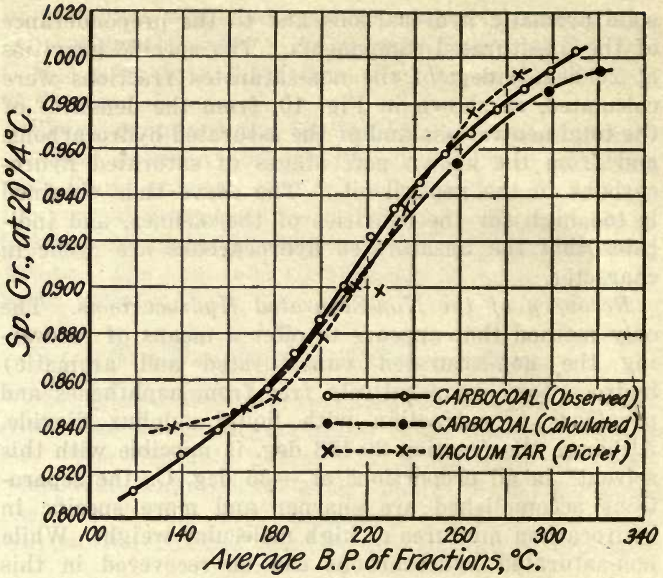

FIG. 11—SPECIFIC GRAVITIES OF NON-SATURATED HYDROCARBONS

gravities and indices of refraction of the seventeen fractions collected were determined. Fig. 11 shows these specific gravities, both observed and calculated, plotted against the average boiling points of the respective fractions.

It was expected that admixture with saturated hydrocarbons would cause the observed values in the lowest-boiling fractions to fall below those calculated. The calculated curve is too incomplete to establish this point, but the "vacuum tar" data also plotted in the figure show the same effect. Although it is very probable that low-boiling saturated hydrocarbons were present in this extract, the large number of fractionations to which they were subjected would be effective in eliminating most of them from the restricted fractions selected for analysis as chemical individuals.

The striking resemblance between the non-saturated hydrocarbons from low-temperature tar and "vacuum tar" extends to the respective refractive indices and average molecular weights, which were determined in selected fractions by the usual Beckmann cryoscopic method. The close agreement between the physical constants of these hydrocarbons shows that the non-saturated compounds from the former apparently belong in general to the same class of cyclic, unsaturated hydrocarbons described by Pictet.[1] In this series he was able to identify dihydro-*m*-xylene, dihydromesitylene, dihydroprehnitene and hexahydrofluorene. The higher-boiling members of the series have from three to five double bonds (basis of molecular refraction), and are apparently polycyclic. No aromatic hydrocarbons were detected.

Aromatic Hydrocarbons in the Non-Saturated Oils. The very low congealing temperatures of all of the fractions demonstrate the absence of solid aromatic hydrocarbons of the type occurring in ordinary high-temperature coal tar. Evidence also is not lacking to indicate that no considerable percentage of liquid aromatic hydrocarbons can be present. The densities and indices of refraction of the non-saturated hydrocarbons are notably lower than the corresponding constants of aromatic hydrocarbons of the same boiling point. Moreover, close conformity has been demontrated between the physical properties of the non-saturated hydrocarbons of Carbocoal tar and a series of unsaturated, cyclic compounds among which no aromatics were detected.

Summary

(1) A commercial low-temperature tar has been compared with coke-oven and gas-works tars. The density and "free carbon" content of the crude, dry tars and the density, "free carbon" and air melting point of the pitches remaining after fractional distillation under similar conditions have been determined. The values for the low-temperature tar have been shown to be notably lower than the corresponding figures obtained for the coke-oven and gas-works tars. The fractionation curves of the three tars, however, are very similar.

(2) The phenols have been extracted from each fraction and estimated gravimetrically. The percentages of phenol and the cresols have been found by methods involving nitration and the determination of specific gravities and freezing points. Derivatives of the naphthols are present, but α- and β-naphthol are absent.

(3) The percentage of phenols in low-temperature tars increases with the yield of tar from the coal carbonized, the quantity of non-phenolic oil remaining relatively constant. In general, coals of the highest volatile content yield the most phenols.

(4) The nitrogen bases are 80 per cent tertiary, 20 per cent secondary, and contain no primary compounds. Both types show unsaturation. No preponderant compound is present. Pyridine has been detected in the first fraction, but the higher boiling bases differ from those in ordinary coal tar in that they have lower densities and higher molecular weights. These differences are ascribed to the presence in the low-temperature bases of partly hydrogenated nuclei and of side-chains longer than those characterizing high-temperature bases.

(5) Contrary to the "vacuum tar" of Pictet, low-temperature tar contains no alcohols.

(6) Hydrogen sulphide is present in the lowest fractions, but carbon disulphide is absent. Thiophene is indeterminate in the presence of unsaturated hydrocarbons, which can not be removed.

(7) The neutral oils derived from low-temperature tars are characterized by low density and viscosity, and by the absence of more than traces of compounds solid above —30 deg. C. No single hydrocarbon preponderates in quantity. Unsaturated hydrocarbons are present, and on standing cause darkening and gradual increase in density of the oils. By the use of 98 per cent sulphuric acid, the saturated and non-saturated hydrocarbons have been separated. Correction is made for polymerization. The proportion of naphthenes has been determined from the specific gravities of the residual saturated hydrocarbons.

(8) The non-saturated hydrocarbons recovered by liquid sulphur dioxide have been shown by determinations of density, index of refraction and molecular weight to belong to the same series of cyclic unsaturated hydrocarbons as those occurring in "vacuum tar." Solid aromatic hydrocarbons are absent; liquid aromatic hydrocarbons can be present only in traces.

Examination of Low-Temperature Coal Tar

II. The Mechanism of Coal Carbonization

Critical Review of Current Theories of Secondary Carbonization Reactions—Interpretation of the Mechanism of Coal Carbonization in the Light of the Composition of a Commercial Low-Temperature Tar—A Theory of the Constitution of Coal

IN A previous contribution a scheme was outlined for the ready examination of low-temperature coal tar, and by its means the characteristics of a commercial product were determined. Comparison with the composition of low-temperature tars produced on a small scale shows that the commercial tar represents a slightly more advanced stage of carbonization. It is thus possible in the present paper to present a new viewpoint on the much-disputed mechanism of the carbonization of coal, and to interpret distillation reactions in the light of the composition of this intermediate product. Finally, there is proposed briefly a theory of the constitution of coal which explains the composition of low-temperature tars.

Berthelot's classic theory[34] of the origin of ordinary coal tar held the field for many years after it was first advanced in 1866. Acetylene is formed, Berthelot stated, by the decomposition of such simple gases as methane in the volatile products from coal, and polymerizes immediately at high temperatures to form benzene, styrolene, naphthalene and other aromatic hydrocarbons. This theory has been rendered untenable, however, by experiments which have proved (1) that acetylene is not formed in any considerable quantity in the gaseous products of coal distilled at various temperatures, and that its reaction velocity of synthesis is not fast enough to account for this absence;[35] (3) that methane, ethane and propane do not yield acetylene as their principal decomposition

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[34] Berthelot, *Ann. chim. phys.* [3], vol. 67, p. 53 (1863); [4], vol. 9, pp. 413, 455 (1866); [4], vol. 12, pp. 5, 122 (1867); [4], vol. 16, pp. 143, 148, 153, 162 (1869).

[35] M. J. Burgess and R. V. Wheeler, *J. Chem. Soc.*, vol. 97, p. 1917 (1910); vol. 99, p. 649 (1911); vol. 105, p. 131 (1914); A. H. Clark and R. V. Wheeler, *ibid.*, vol. 103, p. 1704 (1913).

products;[36] and (3) that primary distillation products of relatively high molecular weight—i.e., low-temperature tars—are obtained in the carbonization of coal.

All modern theories of carbonization, therefore, acknowledge the important rôle played by low-temperature tars in the distillation of coal. While it is thus generally recognized that ordinary high-temperature (900-1,200 deg. C.) coal tar is formed by the decomposition of tar produced at lower temperatures (500-600 deg. C.), the mechanism of this decomposition[37] is still a matter of lively dispute. No comprehensive scheme has been advanced to account for more than relatively a small number of carbonization phenomena. Investigators in general have confined themselves to limited aspects of the problem, and have sought to lay emphasis upon certain predominating reactions. Thus, the origin of the aromatic hydrocarbons of ordinary tar has been variously attributed to:

(1) Decomposition of the hydrocarbons of low-temperature tar to simple compounds, which subsequently undergo pyrogenetic syntheses (Jones, Bone, *et al.*).

(2) Hydrogenation and dealkylation of the phenols of low-temperature tar (Schulze, Fischer and Schrader).

(3) Dehydrogenation and dealkylation of the unsaturated hydrocarbons of low-temperature tar (Pictet).

The present investigation leads to evidence which supports in general the last two of these conceptions, and hence assigns to pyrogenetic syntheses a part of secondary importance. A brief review of the experimental data underlying these several carbonization theories is a necessary preliminary to the development of a more comprehensive and extended analysis of the phenomena of coal distillation.

THEORIES OF DECOMPOSITION OF LOW-TEMPERATURE HYDROCARBONS

Pyrogenetic Syntheses. Probably the most generally accepted theories of tar formation at present are those which postulate the decomposition of the primary

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[36] T. E. Thorpe and J. Young, *Proc. Roy. Soc.*, vol. 21, p. 184 (1873); H. E. Armstrong and A. K. Miller, *J. Chem. Soc.*, vol. 49, p. 74 (1886); F. Haber, *Ber.*, vol. 29, p. 2691 (1896); W. A. Bone and H. F. Coward, *J. Chem. Soc.*, vol. 93, p. 1197 (1908).

[37] *Cf.* the analogous process of decomposition of the bitumen of shale to yield oil on distillation, R. H. McKee and E. E. Lyder, *J. Ind. Eng. Chem.*, vol. 13, pp. 613, 678 (1921); Arthur J. Franks, CHEM. & MET. ENG., vol. 25, pp. 731, 778 (1921); C. W. Botkin, *ibid.*, vol. 24, p. 876 (1921); L. C. Karrick, *Chem. Age* (N. Y.), vol. 30, p. 112 (1922).

tar to simple unsaturated hydrocarbons that condense subsequently to form aromatic hydrocarbons. Jones[38] states that "the mechanism of the breaking down of low-temperature tar consists essentially in the decomposition of the naphthenes, paraffines and unsaturated hydrocarbons present in the low-temperature tar to form olefines of varying carbon content, which condense at higher temperatures to aromatic substances."

In arriving at this conclusion he passed low-temperature tar[39] slowly through a tube filled with porous porcelain, and examined the gaseous products obtained at various temperatures between 550 and 800 deg. C. He stated that benzenoid hydrocarbons could be formed only to a limited extent[40] by the elimination of hydrogen from the corresponding naphthenes, since members of the cyclohexane series break down principally by a scission of the ring with the formation of olefines, including butadiene, and of paraffines and hydrogen. The gaseous olefines were found to be at a maximum at 550 deg., and almost disappeared at 750 deg. This disappearance synchronized with the appearance of naphthalene, and immediately preceded a rapid increase in the evolution of hydrogen, which "must probably be attributed to the union of the aromatic molecules and to intramolecular ring closing."

Jones quotes the work of Staudinger[41] as an example of the polymerization of diolefines to aromatic substances. Moreover, Staudinger identified butadiene in the gas distilled from coal. Instances of its formation also from naphthenes, olefines, saturated hydrocarbons and petroleum vapors from cracking stills are also cited. "It is highly probable," Jones concludes, "that a necessary transition stage is the formation and condensation of olefines containing the conjugated double linkage —CH: CH. CH: CH— . Polynuclear aromatic substances are formed at 750 deg. and upward subsequent to the decomposition of the olefines." Jones, contrary to Pictet, regards phenols as primary products of coal distillation, "those of high-temperature tar being formed with certain changes from those of low-temperature tar. Much of the high-temperature pitch is formed by partial carbonization of the low-temperature pitch."

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[38] D. T. Jones, *J. Soc. Chem. Ind.,* vol. 36, p. 3 (1917).

[39] D. T. Jones and R. V. Wheeler, *J. Chem. Soc.,* vol. 105, p 140 (1914).

[40] D. T. Jones, *J. Chem. Soc.,* vol. 107, p. 1582 (1915).

[41] H. Staudinger, R. Endle and J. Herold, *Ber.,* vol. 46, p. 2466 (1913).

Bone,[42] from a study[43] of the behavior of the simple hydrocarbons at temperatures between 500 and 1,200 deg. C., has elaborated this theory of olefine condensations. He introduces the new conception that the thermal decomposition of the hydrocarbons of low-temperature tar "involves the *primary* formation by dehydrogenation of the unsaturated residues CH_2 (two free bonds) and CH (three free bonds), which during a fugitive but really independent existence are free to interact with the surrounding gaseous medium after their kind." Bone points out that the most favorable temperature range for aromatic formations from such residues (500-800 deg.) coincides with that giving the best yields of benzene and its homologs and is well below that which is most favorable to the hydrogenation of the residues to methane. Between 500 and 800 deg. "ethylene is, by reason of its rapid production of CH residues (three free bonds) during its primary decomposition, eminently capable of generating aromatic nuclei, although to a less marked degree than in the case of acetylene. On the other hand, ethane, which primarily produces CH_2 residues (two free bonds) only, does not form aromatic nuclei so readily as does ethylene."

Another variation of the olefine theory is advocated by Whitaker and Crowell,[44] who distilled coal in 5-lb. charges at different temperatures, and examined the liquid and gaseous products of carbonization. They suggest that the course of reactions in coal carbonization is as follows: "Solid coal→high molecular weight paraffines→low molecular weight paraffines; olefines→acetylenes, naphthenes and polycyclic compounds→benzene and its homologs→higher homologs of benzene →xylene→toluene→benzene, etc." Attention was directed to the apparent marked similarity between this series of decompositions and those postulated[45] for oil cracking. A somewhat similar sequence of coal reactions has recently been advanced by Wigersma.[46]

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[42] W. A. Bone, "Coal and Its Scientific Uses" (London, 1918), p. 143 *et seq.*

[43] W. A. Bone and H. F. Coward, *J. Chem. Soc.*, vol. 93, p. 1197 (1908).

[44] M. C. Whitaker and W. H. Crowell, *J. Ind. Eng. Chem.*, vol. 9, p. 261 (1917).

[45] *Cf.* publications by Rittman, Zanetti, Egloff, Leslie *et al.* in *J. Ind. Eng. Chem.* A very extensive review of the literature to 1916 on the pyrogenesis of hydrocarbons is given by E. L. Lomax, A. F. Dunstan and F. B. Thole, *J. Inst. Pet. Tech.*, vol. 3, p. 36 (1916); *cf.* W. Gluud, *Ges. Abhandl.*, vol. 2, p. 261 (1917).

[46] B. Wigersma, *Chem. Weekblad*, vol. 16, p. 1356 (1919).

THEORY OF THE DECOMPOSITION OF LOW-TEMPERATURE PHENOLS

The investigators whose work has been reviewed thus far have paid scant attention to the rôle of the phenols in secondary decompositions. In 1885 Schulze,[47] on the occasion of his pioneer investigation of the naphthols of ordinary coal tar, stated that coal is essentially altered cellulose and that its primary decomposition products are the phenols. The phenols on further heating (1) eliminate water to synthesize high-boiling hydrocarbons; (2) are partly reduced to low-boiling hydrocarbons; (3) are decomposed to form gases; or (4) escape unchanged. These reactions were conceived as progressing simultaneously and in equilibrium with each other. So strong was the influence of Berthelot's theory at that time, however, that Schulze made his propositions simply to supplement rather than to displace the acetylene hypothesis.

Very recently Fischer and Schrader[48] have also assigned to the phenols a part of major importance. They point out that low-temperature tars consist essentially of hydrocarbons similar to those of petroleum and of phenols, but contain no aromatic hydrocarbons. The benzene homologs in high-temperature coal tar must be formed from these phenols, they conclude, since the hydrocarbons can be converted into aromatics only to a slight extent. In support of this view experiments are cited on the decomposition of cresols and xylenols when passed through tinned tubes heated to 750 deg. in an atmosphere of hydrogen. The phenols were reduced to benzene homologs, and these in turn yielded some benzene. Thus, according to these authors' theories of the decomposition of low-temperature tar in coal carbonization, the aliphatic hydrocarbons are broken down into gases, while the hydroaromatic hydrocarbons are in part dehydrogenated and in part changed into gaseous hydrocarbons. A small portion of the phenols of the low-temperature tar remain unchanged, but most of them are reduced to such stable hydrocarbons as benzene, or take part in syntheses of napthalene, anthracene and other aromatics.

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[47] K. E. Schulze, *Lieb. Ann.*, vol. 227, p. 143 (1885).

[48] F. Fischer and H. Schrader, *Brennstoff Chem.*, vol. 1, pp. 4, 22 (1920); vol. 2, p. 37 (1921).

THEORY OF DEHYDROGENATION AND DEALKYLATION

Pictet[49] passed "vacuum tar" through a red-hot tube filled with pieces of coke, and obtained the typical products of high-temperature distillation. He concluded that the hydroaromatic hydrocarbons of vacuum tar underwent dehydrogenation and detachment of side-chains to yield aromatic hydrocarbons and the large quantity of hydrogen and methane homologs characteristic of high-temperature gases. This theory is supported by the known tendency of aromatic hydrides to lose a part of their hydrogen, by the occasional presence in ordinary tar of small quantities of hydroaromatic hydrocarbons, and by the fact that the cracking of naphthenic petrols yields a certain quantity of aromatic hydrocarbons. Since cyclohexane on cracking yields little benzene, and tends rather to break the ring with the formation of unsaturated aliphatic compounds, the cyclanes of coal, Pictet states, cannot have contributed largely to the formation of benzene and its homologs.

It is the unsaturated cyclic hydrocarbons, he argues, which are present in much larger quantity, and which are hence the principal source of the benzene hydrocarbons of ordinary tar. Certain of the polycyclic hydrocarbons, such as fluorene, also owe their existence to simple dehydrogenation, since hexahydrofluorene was found in "vacuum tar." The origin of naphthalene and anthracene was regarded as still obscure, however, since no hydrogenated derivative of either of these was found in "vacuum tar" or in the benzene extract of coal.

LIMITATIONS OF EXPERIMENTAL METHODS IN CARBONIZATION STUDIES

It is desired to call attention at this point to certain conditions which complicate the study of carbonization reactions. Aside from such factors of prime importance as temperature and pressure, the course which these reactions take depends upon the relative concentrations of the reacting substances, and hence the nature of the coal carbonized, and upon the path of travel of the gases in the oven.[50]

Coals of oxygen content lower than normally used in commercial carbonization practice have been employed by some observers, who consequently lost sight of the

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[49] A. Pictet, *Ann. chim.* [9], vol. 10, p. 322 (1918).

[50] *Cf.* G. E. Foxwell, *J. Soc. Chem. Ind.*, vol. 40, pp. 193T, 220T (1921).

effect which the higher phenol concentration would have in the formation of the typical aromatic hydrocarbons of ordinary tar. Carbonization reactions occur simultaneously, and represent complex equilibria, the individual factors of which are difficult to divorce from one another for separate investigation. When experiments on the decomposition of isolated hydrocarbons are quoted, translation of such results to commercial conditions is obviously open to question. The strongly reducing atmosphere of coke ovens and gas retorts is a factor that too often has been ignored in pyrogenetic assumptions. Thus it has been shown[51] that at 550 deg. benzene in an atmosphere of nitrogen readily loses hydrogen with the formation of diphenyl, but in the presence of an excess of hydrogen yields only traces of diphenyl. Toluene carried through coke in a stream of nitrogen at 750 deg. yields naphthalene, anthracene and a viscous black liquid. On the other hand, the substitution of hydrogen for nitrogen greatly accelerates the decomposition of the toluene, and produces large amounts of benzene and only a small quantity of solid condensate.

Attention is directed also to the difference in the results obtained in small-scale experiments and in commercial operation. For example, when 2-g. samples of coal are distilled[52] under a high vacuum in a platinum tube, there is obtained a maximum yield of tar at 750 deg., which is nearly four times that recovered at 450 deg. It is a well-known fact, on the other hand, that the yield of low-temperature tars on a commercial scale is about double that of ordinary high-temperature tars.

Again, Jones[38] decomposed 0.1-g. samples of low-temperature tar in a glass tube filled with porous porcelain, and based much of his theory of carbonization reactions on the analysis of the gases obtained at different temperatures. If comparison is made of these results with the gas analyses of Thau,[53] who distilled coal in a commercial coke oven over the same range of temperatures, striking differences are at once manifest. The sudden increases in the evolution of hydrogen and of methane synchronizing with the disappearance of olefines and the appearance of aromatics noted by Jones is not

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[51] J. W. Cobb and S. F. Dufton, *Chem. Trade J.*, vol. 63, p. 197 (1918); *Gas World*, vol. 69, p. 127 (1918); *Gas. J.*, vol. 143, p. 482 (1918).

[52] M. J. Burgess and R. V. Wheeler, *J. Chem. Soc.*, vol. 97, p. 1917 (1910); vol. 99, p. 649 (1911); vol. 105, p. 131 (1914).

[53] O. Thau, *Brennstoff Chem.*, vol. 1, pp. 52, 66 (1920).

apparent in the coke-oven analyses. As an example of the influence of retorting conditions, Thau found as a result of superheating the upper part of his coke oven that the hot surfaces of carbon were much more effective in causing decomposition than were the retort walls.

Interpretation of Carbonization Reactions in Terms of the Present Investigation

The low-temperature tar studied in the present investigation represents a stage of carbonization slightly more advanced than that which gave rise to the vacuum tars investigated by Pictet and by Jones and Wheeler. It was produced by the Carbocoal process[54] in a commercial retort that afforded an opportunity for secondary reactions to take place to a limited extent. Thus the distillation vapors came into contact with the retort shell heated to about 600 deg., and yielded a product that is distinguished from these true low-temperature tars by (1) a slight decrease in the quantity of total phenols and a marked increase in the proportion of low-boiling phenols; (2) the appearance of a large percentage of tertiary nitrogen bases; and (3) a notable increase in the ratio of unsaturated to saturated hydrocarbons.

THE DECOMPOSITION OF LOW-TEMPERATURE PHENOLS DURING CARBONIZATION

A true low-temperature tar contains about ten times the quantity of phenols that appears ultimately in the high-temperature tar. Thus, a 30 per cent volatile coal produces a primary tar containing about one-quarter its weight of phenols, and yields in the coke oven about half this weight of tar containing less than 5 per cent of phenols. The low-temperature phenols consist principally of the higher homologs. High-temperature phenols, on the other hand, contain about two parts of cresols to one of phenol, together with a relatively insignificant proportion of higher-boiling tar-acids. It is thus apparent that while the phenolic components of the primary tar contribute very largely to the formation of secondary products, only a small part of them survive as phenols, and then chiefly as the first members of the series.

The low-temperature phenols, as would be expected,

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[54] See p. 6 for a description of the conditions of carbonization in the Carbocoal process.

occupy a position intermediate between the extreme low-temperature type and the phenols of ordinary tar. The phenols obtained[55] by steam distillation of a Lohberg gas coal at a temperature slightly lower than that in the case of the low-temperature phenols exceeded the latter in total quantity. The fraction of Lohberg phenols distilling below 230 deg. constituted only 7 per cent of the total weight, while the corresponding fraction of low-temperature phenols amounted to 57 per cent. It thus becomes evident that the first stage in the decomposition of the primary phenols is one which involves principally the elimination of the multiple short sidechains of the higher homologs. This reaction is probably accomplished by the replacement of the methyl or ethyl groups by hydrogen from the retort gases, with the formation of methane or ethane.

Again, when low-temperature phenols are passed through a tinned tube at 750 deg. in an atmosphere of hydrogen, there are obtained[48] low-boiling phenols and hydrocarbons, together with water. Higher temperatures, therefore, must eliminate the hydroxyl groups also, and the predominating reaction then becomes hydrogenation with the production of water. Moreover, cresol when passed over coke at 750 deg. in a stream of hydrogen yields benzene and toluene.[51]

The present investigation has shown that the low-temperature phenols contain about 10 per cent of naphthol derivatives. The hydrogenation of these with elimination of water is obviously one source of the naphthalene of high-temperature tar.

If the decomposition of the primary, monocyclic phenols were confined to such hydrogenation reactions, however, there would result in high-temperature tar a much higher yield of light oils and solvent naphtha than is actually the case. Experiment has shown[51] that monocyclic aromatic hydrocarbons also undergo the same reaction—e.g., xylene is converted into toluene, and toluene is converted into benzene, with the simultaneous formation of a small amount of solid condensate. Thus it was found[44] that the temperatures of maximum formation of xylene, toluene and benzene are respectively 600, 700 and 800 deg., and that the total quantity of light oil formed decreases steadily as the temperature of carbonization is increased above 500 deg. The limited quantity of benzene itself occurring in high-temperature tar, however, makes it neces-

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[55] F. Fischer, *Brennstoff Chem.*, vol. 1, pp. 31, 47 (1920).

sary to conclude that in addition to the reactions enumerated, a portion of the benzene participates in pyrogenetic syntheses. It is possible also that some of the phenols sustain scission of the ring and are lost from the tar as gases, or, as Fischer and Schrader[48] suggest, condense to form polycyclic aromatic hydrocarbons. However this may be, it is nevertheless evident that the phenols are the chief source of the monocyclic aromatic hydrocarbons.

THE DECOMPOSITION OF THE NITROGEN BASES DURING CARBONIZATION

Since a considerable quantity of the nitrogen bases of low-temperature tars remains after distillation in the pitch, it is difficult to determine whether the total quantity is greater or less than in ordinary tar. It was found,[56] however, that the percentage of bases (3.42 per cent) boiling under 326 deg. in a mixture of coke-oven and gas-works tar was nearly double that (1.94 per cent) of the low-temperature tar. It is probable, therefore, that low-boiling bases are formed from high-boiling bases in a manner analogous to the decomposition of the high-boiling phenols.

Pictet's suggestion[49] that quinoline is formed from dihydroquinoline by simple dehydrogenation seems to be the most rational explanation of the primary decompositions of the low-temperature bases. Secondary bases of the type of dihydroquinoline are found in "vacuum tar," but tertiary bases are absent. The fact that 80 per cent of the low-temperature bases and almost all of the high-temperature bases are tertiary compounds supports this theory of dehydrogenation.

Experiments with the low-temperature bases demonstrated the presence of unsaturated bases, the relative molecular weights[57] of which average 10 to 15 higher (Fig. 12) than the values of the corresponding high-temperature compounds. At higher temperatures (700 to 800 deg.), therefore, a process of combined dehydrogenation and dealkylation must take place to yield the ordinary bases such as quinoline and acridine. Moreover, the toluidines described by Pictet then yield the aniline of ordinary tar just as it has been shown that cresol yields phenol, and toluene yields benzene.

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[56] See first paper in this series.

[57] Only relative values are given by the ordinary Beckmann cryoscopic method, since nitrogen bases are slightly associated in benzene solution.

The low-temperature distillate was shown to contain no preponderating base, but to represent a series of compounds of increasing molecular weight. The distillation curves of Fig. 13 emphasize the preponderance of quinoline in the high-temperature bases, and indicate, if this theory is accepted, that the bulk of the middle-boiling bases of low-temperature tar are structural derivatives of quinoline, and yield this compound upon decomposition at the temperature of the coke oven. The physical constants obtained are consistent wtih this observation, and dihydroquinoline has been identified in "vacuum tar."

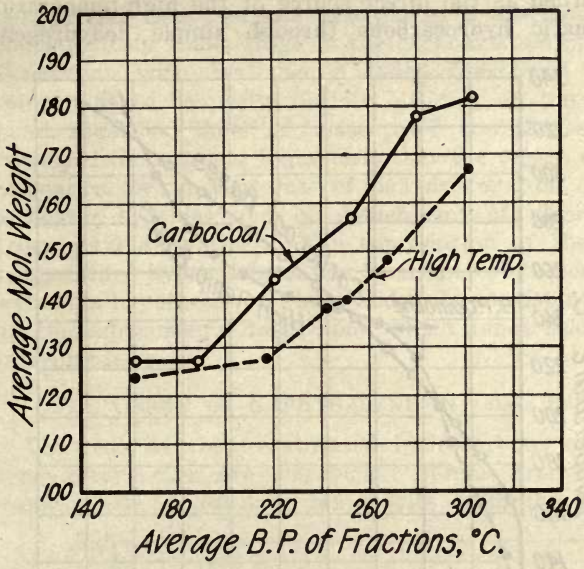

FIG. 12—AVERAGE MOLECULAR WEIGHTS OF BASES

The Decomposition of the Hydrocarbons During Carbonization

The ratio of saturated to unsaturated hydrocarbons is highest in the tars produced under high vacuum at the lowest temperatures. Thus the saturated hydrocarbons obtained by Jones and Wheeler were about equal in quantity to the non-saturated, while in low-temperature tar they formed only one-third of the distillate and a much smaller fraction of the entire tar. The obvious conclusion, therefore, is that the initial decomposition of the primary hydrocarbons is characterized by a partial dehydrogenation of the naphthenes to form hydroaromatics.

As mentioned above, Jones[40] was led to believe from his experience in the decomposition of cyclohexane, methylcyclohexane and the di- and tetrahydro-derivatives of naphthalene that the naphthenes cannot be regarded as the direct source of the high-temperature aromatic hydrocarbons through simple dehydrogenation and dealkylation. The large yields obtained of both the corresponding aromatic hydrocarbon and hydrogen were explained on the basis that "the most probable course of the reaction would be for the cyclohexane first to lose two atoms of hydrogen and form cyclohexene, which then decomposes in two ways, yielding benzene and butadiene." The principal reaction and the one contributing most largely to aromatic formation was held to be the condensation of such conjugated unsaturated nuclei as the butadiene represents. These nuclei are stated to result in the distillation of coal from the decomposition of the paraffines, the

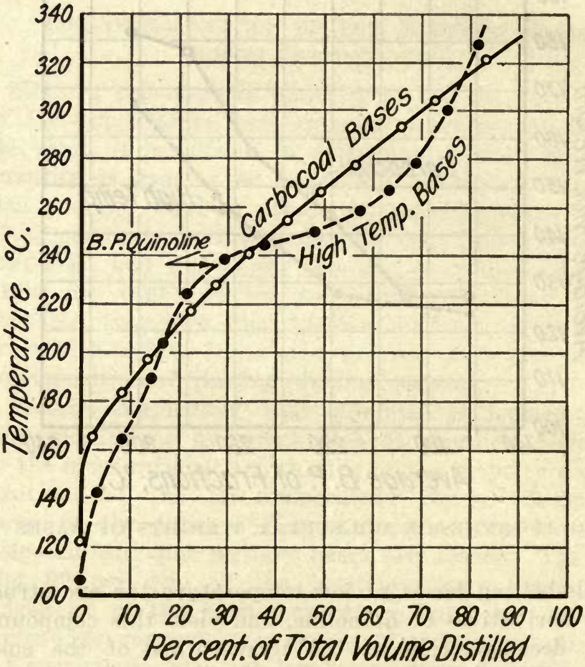

FIG. 13—DISTILLATION OF BASES

naphthenes and the unsaturated hydrocarbons of low-temperature tar.

Results in the present investigation, on the contrary, lead to the contention that while the elimination of hydrogen from the naphthenes of the primary low-temperature tar is the initial step in the decomposition reactions, the intermediate di- and tetra-hydroderivatives thus formed constitute a distinct and comparatively stable stage in the carbonization of coal. Consistent with his theory Jones considered these compounds to be partly olefinic. Pictet, on the other hand, identified them as unsaturated naphthenes, and advanced the rational hypothesis that the origin of the aromatics lay in a process of dehydrogenation of the aromatic hydrides and of detachment of sidechains from alkyl derivatives. The composition of the low-temperature hydrocarbons has been shown[56] to conform with this hypothesis of Pictet and to be consistent with all the experimental facts upon which Jones bases his interpretation.

THE ORIGIN OF NAPHTHALENE IN COAL TARS

The bulk of the unsaturated hydrocarbons of low-temperature tars are polycyclic. While some of the naphthalene of ordinary tar results from the hydro-

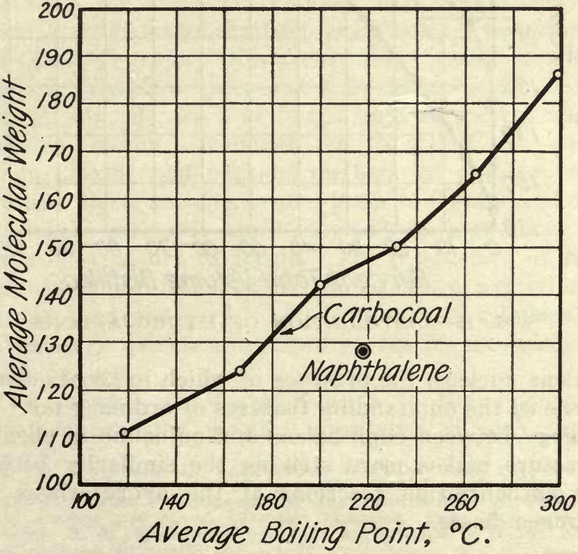

FIG. 14—MOLECULAR WEIGHTS OF NON-SATURATED HYDROCARBONS

genation of naphthols, it is believed that the naphthalene and other polynuclear aromatic hydrocarbons owe their origin chiefly to the decomposition of these polycyclic unsaturated compounds. The presence of a series of homologs of hydrogenated and alkylated bicyclic hydrocarbons is indicated in low-temperature tar by the physical and chemical properties. For example, the average molecular weights[58] of the middle-boiling fractions (Fig. 14) are notably higher than that of naphthalene. Fig. 15 shows that the secondary reactions giving rise to high-temperature tar decompose these bicyclic hydrocarbons to the single stable naphthalene nucleus, the presence of which in large quantity is one of the outstanding features of ordinary tar. The analogy between naphthalene and quinoline in chemical structure makes more striking the similarity between the carbonization reactions of the hydrocarbons and nitrogen bases.

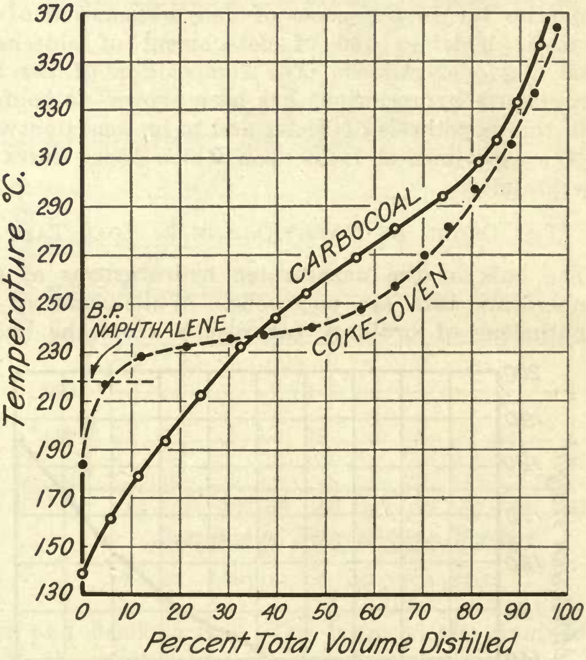

FIG. 15—DISTILLATION OF HYDROCARBONS

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[58] Determined in benzene solution by the Beckmann cryoscopic method.

Probably the most remarkable general characteristic of low-temperature tars is the fact that they are almost entirely cyclic in nature. So far as the various compounds have been identified, moreover, these cycles have shown themselves to be six-membered rings or combinations of six-membered rings. This structural characteristic apparently persists in the tar as the temperature of distillation of the coal is increased.

It seems reasonable, therefore, in view of the great stability of the six-membered ring, to ask if this structure is not characteristic also of the coal substance itself. Such a conception is contrary, of course, to the widely accepted cellulose-furane theory.[59] Fischer and Schrader[60] have recently stated that the plant cellulose is destroyed by bacterial activity in the early stages of peat formation, and pointed out, moreover, that while cellulose yields on decomposition almost exclusively phenol itself, low-temperature tars contain chiefly the higher homologs of phenol. In the absence of cellulose the lignin must hence be the source of the phenols of coal tar.

The cyclic structure of lignin has been advocated by these authors, who assign to it an aromatic configuration with acetyl and methoxyl groups. During coal formation the methoxyl content must eventually decrease through saponification, reduction or replacement by hydroxyl groups. In any case there results a phenol, which is considered identical with humic acid. Oxidation or polymerization of humic acid forms the alkali-insoluble humin. Further splitting off of water, carbon dioxide and perhaps methane at ordinary temperature, these authors argue, leads to lignite and coal. The whole series is thus assumed to perpetuate the aromatic structure of lignin. The production of large amounts of mellitic acid by the pressure oxidation of charcoal and ordinary coals (but not of cellulose) is contributory evidence of the presence of six-membered cycles in coal.

The present investigation leads to the suggestion, therefore, that the chemical properties of coal may be

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[59] D. T. Jones and R. V. Wheeler, *J. Chem. Soc.*, vol. 105, pp. 140, 2562 (1914); vol. 107, p. 1318 (1915); vol. 109, p. 707 (1916); *cf.* also "Monograph on the Constitution of Coal," by M. C. Stopes and R. V. Wheeler (London, Dept. Sci. and Ind. research, H. M. Stationery Off.) for an exhaustive review of the knowledge on this subject in 1918.

[60] F. Fischer and H. Schrader, *Brennstoff Chem.*, vol. 2, p. 37 (1921); *cf.* Klever, Jonas and Keppeler, *ibid.*, vol. 2, p. 213 (1921), and Fischer and Schrader, *ibid.*, vol. 2, p. 237 (1921).

represented by a structure containing many such cycles. This structure may be pictured as an aggregate of "mosaics" of these rings. Some of the "mosaics" contain oxygen, and display the insolubility characteristic of the "cellulosic degradation products,"[59] or, according to Fischer and Schrader, the "lignin degradation products." These may be regarded as polymerized phenols, as suggested above, or as multi-molecular structures in which component rings are joined together by oxygen-containing bridges. Heating results in the breaking of these bridges with the formation of high-boiling phenols, the sidechains of which are remnants of other broken linkages.

Similarly, other "mosaics" may be pictured to represent the same typical rings held together by bridges of paraffine hydrocarbons, the breaking or detachment of which are responsible for the presence of straight-chain hydrocarbons in low-temperature tars,[61] or even in seams of the coal deposits themselves. These structures are more soluble, and have been called the "resinous constituents."[59] Nitrogen and sulphur compounds may be regarded as appearing in strictly analogous configurations.

SUMMARY OF THE MECHANISM OF COAL CARBONIZATION

(1) The decomposition of the coal substance to ordinary high-temperature tar when subjected to the action of heat is a process of progressive, step-by-step decomposition, in which pyrogenetic syntheses play only a secondary part.

(2) Six-membered rings and combinations thereof characterize the entire series of decomposition products from coal to high-temperature tar. The decompositions during carbonization are essentially reactions effecting the elimination of sidechains.

(3) The average molecular weights of the liquid intermediate products constantly decrease as the temperature of carbonization rises. This decrease is marked by the evolution of hydrogen, methane and ethane.

(4) The initial decomposition of the low-temperature tar first formed is brought about by (*a*) loss of hydrogen from a portion of the naphthenes with a resultant increase in the proportion of unsaturated hydrocarbons; (*b*) loss of sidechains from the phenols

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[61] *Cf.* the "bound molecules" of Jones and Wheeler (Ref. 59).

by hydrogenation with the resultant formation of lower-boiling phenols; and (*c*) loss of hydrogen from the nitrogen bases to form a large proportion of tertiary compounds. (This stage is represented by Carbocoal tar.)

(5) Final decompositions are at a maximum between 700 and 800 deg., and are marked by (*a*) dehydrogenation and dealkylation of the hydroaromatic unsaturated hydrocarbons and nitrogen bases to form aromatics, with the elimination of hydrogen, methane and other simple gases; (*b*) hydrogenation of the phenols to aromatic hydrocarbons and of these aromatic hydrocarbons to lower-boiling aromatics, with the formation of methane, ethane and water; and (*c*) secondary pyrogenetic syntheses of higher aromatics from simple compounds.

(6) The phenols of low-temperature tar are the principal source of the monocyclic aromatic hydrocarbons. The unsaturated naphthenes of low-temperature tar are the principal source of the polycyclic aromatic hydrocarbons.

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Vita

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