higher iodine values and lower titers, call for positions nearer the vertex O. The explanation, of course, lies in the presence of a considerable percentage of linoleic acid in the liquid acids of these stocks. The effect of linoleic acid on the shape of the titer surface, of which the constant-temperature lines represent projected contours, has been discussed in Part I of this series (*13*). The position of stock 4 also reflects an appreciable linoleic acid content.

The composition of any mixture of these stocks can be determined graphically on the diagram. Differences in behavior among such mixtures can thus be considered in relation to specific differences in fatty acid composition.

The usefulness of this type of data in the study of plant processes in the fatty acid industries will be readily apparent.

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Examination of the Phenols of a Low-Temperature Coal Tar

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The commercial utilization of low-temperature tar would remove one of the chief obstacles to the establishment of low-temperature carbonization processes in this country. This primary tar is a unique source of high-boiling phenols, concerning whose chemical structure there has been considerable conjecture but little data.

More exact knowledge of the constitution of these phenols would serve to indicate those industrial markets in which they might be utilized as a new raw material. It is now shown that the fraction of these tar acids boiling up to 260° C. consists of homologs of phenol in which the alkyl groups are largely in a meta position to the hydroxyl group. The methods used in separating individual phenols from groups of isomers are presented and two of the phenols are identified as mesitol and 3-methyl-5-ethylphenol.

THE large proportion of high-boiling constituents is a well-known characteristic of low-temperature tar, particularly of the phenolic portion of the distilled tars. Thus the outstanding point of difference between high-temperature or coke-oven tar phenols and the phenols of low-temperature tar is the relative proportion of low- and medium-boiling constituents, as shown in Table I.

TABLE I. COMPOSITION OF COKE-OVEN AND PRIMARY TAR PHENOLS

	180–210° C.	210–225° C.	225–280° C.	280–320° C.	PITCH
	%	%	%	%	%
Coke-oven tar phenols	60	15	10	7	8
Primary tar phenols	9	24	22	15	30

Although the phenols above the xylenol range form approximately 66 per cent of the tar acids of low-temperature tar, no exact knowledge of their constitution or structure is available. The phenols up to and including the xylenol range have been studied by many investigators, but fractions above 225° C. have received little attention.

Gluud and Breuer (*3*) made cresoxyacetic acid derivatives of a fraction boiling from 237° to 241° C. and from the analyses showed that the phenol approximated the formula $C_9H_{12}O$ which they considered indicated trimethylphenol. Avenarius (*1*), however, from consideration of analyses of allophanic acid derivatives concluded that the low hydrogen content indicated presence of unsaturated side chains in this series, as did Weindel (*11*) who made analyses of the acetyl esters. Steinkopf and Höpner (*8*) stated that some of the phenols above the cresols evidently contained side chains longer than the methyl.

Morgan and Soule (*6*) carefully fractionated the whole range of phenols from both a low-temperature tar and a coke-oven tar and plotted curves of specific gravities versus the mean boiling points of the respective fractions. These curves (Figure 1) show a well-defined minimum point and also indicate that the Carbocoal tar phenols are lower in density than the corresponding fractions of coke-oven tar over almost the entire range. Regarding these curves, Morgan and Soule state: "The decrease in specific gravity of the phenols as the boiling point increases indicates the presence of aliphatic side chains 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 increase in the viscosity of the fractions mark the appearance of α- and β-naphthols in the high-temperature phenols, and bicyclic compounds at least in the low-temperature phenols."

PREPARATION OF FRACTIONS

In the present investigation the phenols boiling from 220° to 260° C. have been examined, particularly to determine the changes in composition responsible for the shape of the specific gravity–boiling point curve as noted by Morgan and Soule (*6*)—i. e., the inflection point—and the appreciable differences in density of corresponding fractions of the phenols of high- and low-temperature tar. The tar acids studied were obtained from a low-temperature tar produced during some large-scale tests on the Doherty complete gasification process at Toledo, Ohio, May to November, 1925. This tar is usually known as Hydrogas tar.

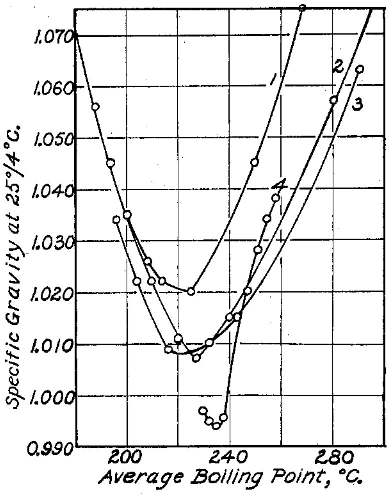


Figure 1. Boiling Point *vs.* Specific Gravity of Fractions of Phenols from Various Tars

1. Coke-oven tar phenols (Morgan and Soule)
2. Carbocoal tar phenols (Morgan and Soule)
3. Hydrogas tar phenols (Morgan and Meighan)
4. Low-temperature tar phenols (present investigation)

The crude primary tar was distilled from a 1000-gallon (3785-liter) still to a pitch residue of 71° C. melting point, and the phenols were extracted from 1464 gallons (5541 liters) of distillate with caustic soda, care being taken to eliminate hydrocarbon oils from the phenolate solution by agitation with benzene followed by steam distillation. In order to split up the whole range of tar acids into smaller fractions, the acids were fractionally distilled under reduced pressure using a 50-gallon (189-liter) iron still with a fractionating column, 6 feet (180 cm.) long and 6 inches (15 cm.) in diameter, filled with 1-inch (2.5-cm.) Raschig rings. During the distillation the pressure averaged 53 mm.

Table II. Analysis of Tar

Sp. gr. at 25/25° C.	1.03
"Free carbon"	0.71%
Distillation end point at 50 per cent off by volume	330° C.
Pitch melting point (cube-in-water) at 50 per cent off by volume	40° C.
Sp. gr. of distillate at 25/25° C.	0.96
Tar acid content of distillate	21.6%
Nitrogen bases in distillate	3.0%
Sp. gr. of neutral oil at 25/25° C.	0.91
Sulfonation residue, per cent of neutral oil	30.0

Great attention was paid to efficient fractionation, without which the separation by distillation of even fairly simple mixtures is valueless and misleading. After several tests a fractionating column was finally designed that gave excellent results. This was a modification of the column described by Peters and Baker (*7*). Using this column at atmospheric pressure, several of the cuts obtained in the large-scale distillation *in vacuo* were subjected to repeated fractionations. In the first fractionation, two 15° cuts were separated. The first, boiling at 225° to 240° C., was selected because it contained the phenol corresponding to the minimum point of the specific gravity–boiling point curve, while the fraction boiling at 240° to 255° C. was taken as being well up on the rising part of this curve and hence in the range in which clues might be found to account for the difference in density of corresponding fractions of high- and low-temperature tar phenols. During the succeeding fractionations the cuts were made narrower and narrower, until in the sixth and final distillation of the original 225° to 240° C. cut 0.5° cuts were taken, as was also the case in the fifth and last fractionation of the 240° to 255° C. portion. The largest fraction obtained boiled at 234° to 234.5° C., which coincides with the point of minimum density, so that this fraction was used for the attempt to isolate individual compounds and to study their chemical structures.

That the fractionation of the tar acids used in this work was fairly efficient is evidenced by the fact that the specific gravity–boiling point curve (Figure 2) shows to a slight extent the irregularities obtainable by splitting a complete set of isomers into its constituents or into several groups of constituents.

During each fractionation of the two 15° cuts, "spot cuts," consisting of a few drops each, were taken at close intervals for the determination of refractive indices. The curves obtained by plotting these data assisted in following the progress in separation made by each fractionation, and the curves for the final fractionations are shown in Figure 2 together with a curve of specific gravities of the individual cuts. It will be observed that both the refractive index and the specific gravity curves show distinct minima, as in the curve of Morgan and Soule. This point of inflection was considered by Curtis and Beekhuis (*2*) to indicate the appearance above that point of dihydric phenols in appreciable quantity.

Characteristics Studied

Dehydrogenation and Deoxygenation. Partial hydrogenation of the nucleus is one of the possible differences of structure that might account for the observation of Morgan and Soule that phenols of low-temperature tar have lower densities than phenols of the same boiling point from high-temperature tar. In order to test this point, several fractions between 250° and 260° C. were passed over a nickel-thoria catalyst at 350° C. The gas liberated was negligible, whereas with tetrahydronaphthol and tetrahydronaphthalene almost theoretical yields of hydrogen were obtained, together with naphthol in one case and naphthalene in the other. This excludes the possibility of the presence of polynuclear phenols, since the naphthols themselves boil above 280° C., whereas the failure to liberate hydrogen rules out the hydrogenated naphthols.

By deoxygenation the parent hydrocarbon can be obtained. An active carbon catalyst in the presence of hydrogen was found to give better results and at a lower temperature than the classical zinc-dust method of Baeyer. In each case only small yields of hydrocarbons were obtained and these were mixtures of a number of compounds as indicated by the wide boiling range, so that no definite conclusions could be drawn from these tests.

Solid Derivatives. Attempts were then made to prepare various solid derivatives in order to characterize the phenols more definitely and to aid in the separation of isomers by fractional crystallization. The phenoxyacetic acids, by reaction of the phenols with chloroacetic acid, had been employed by Gluud and Breuer (*3*) in the identification of the lower-boiling phenols of low-temperature tar and had later been applied by Steinkopf and Höpner (*8*) to the xylenols. However, when this method was used with the higher-boiling liquid fractions of tar acids being studied in the present investigation, the reactions were violent and the products consisted largely of noncrystallizable oils. Much more satisfactory results were had with the preparation of the phenylurethans and naphthylurethans, which were also employed by Steinkopf and Höpner. Molecular weight determinations and ultimate analyses of the urethans indicated that the fraction boiling at 234° C. could be represented by the formula $C_9H_{12}O$. Bromo derivatives of the 234° C. fraction were obtained in crystalline form and on analysis confirmed the formula $C_9H_{12}O$ for this cut.

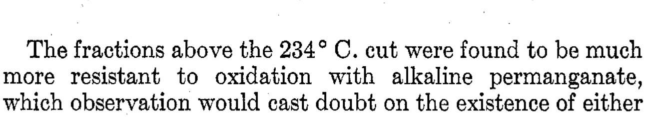
Molecular Weights of Fractions. The molecular weights of the phenol fractions were determined indirectly by the cryoscopic method using the methyl ether of the phenol in benzene solution. This method was found to be more reliable and accurate than the hydrogen equivalent method, using sodium and the toluene solution of the free phenol (*5*). After the third distillation the molecular weights of all of the 5° C. fractions were determined. Unusually high values obtained for the fraction 220° to 225° C., which is in the xylenol range, showed that a large percentage of phenols of molecular weight higher than 122 must be present in this fraction. This fraction was therefore examined more thoroughly and the trimethylphenol, mesitol, separated from the xylenols by the method given below.

Separation by Fractional Liberation and Extraction. The degree of hydrolysis of the sodium salt of a phenol in aqueous solution, and the partition of the phenol itself between two solvents, such as ether and water, are known to be functions of the chemical constitution of the phenol considered. Fractional precipitation by successive addition of small portions of acid to the sodium phenolates has been applied to the separation of phenols, cresols, and xylenols by previous workers. Vavon and Zaharia (*9*) examined various synthetic phenols and found that all phenols could be extracted by ether from the aqueous solution of their sodium salts. The percentage of phenol that was extracted by the ether varied greatly according to the constitution of the phenol. Notably many ortho and diortho compounds were almost completely extracted by the ether in one extraction, demonstrating the high degree of hydrolysis of their sodium salts. A more recent paper on the use of this method presents quantitative data for a number of phenols and indicates commercial possibilities (*4*).

A method of separation combining fractional precipitation and extraction by ether of the phenols from their sodium salts was used in the examination of the phenols boiling over the range 220° to 225° C., proving them to consist of a mixture of mesitol and xylenols. The mesitol was identified by preparation of the dibromide, and by mixed melting point of this with a synthetic specimen of mesitol dibromide.

Oxidation of Side Chains. Although the fractions examined evidently consisted of homologs of phenol, the number, position, and length of the alkyl side chains were yet to be determined, with the evidence strongly in favor of a single long side chain for the 234° C. fraction, since it occurred at the inflection point of the specific gravity and refractive index curves. For this determination, recourse was had to conversion of the alkyl groups into carboxyl groups.

The fraction boiling at 234° C. was in this way converted to a dicarboxymethoxy derivative whose identity with 1-methoxy-3,5-dicarboxybenzene was proved by a mixed-melting-point determination with a sample of this acid obtained synthetically from another source. Since the original tar acid has been shown by several different methods to consist largely of a phenol having the formula $C_9H_{12}O$, the latter must be *m*-methylethylphenol.



The fractions above the 234° C. cut were found to be much more resistant to oxidation with alkaline permanganate, which observation would cast doubt on the existence of either long side chains or unsaturated side chains on the nucleus of these higher boiling phenols.

PROBABLE COMPOSITION OF TAR ACIDS 235° TO 260° C.

Every test that has been applied to the fractions of these low-temperature tar acids up to 260° C. has failed to show any structural differentiation between them and the corresponding fractions of tar acids from high-temperature tar. A series of cuts of the high-temperature tar phenols were prepared for this comparison from a 10-gallon (37.85-liter) sample of "carbolic tar"—the still residue of coke-oven tar phenols after removal of the cresols and xylenols—which was obtained through the courtesy of the Barrett Company. But nevertheless there remain to be explained the marked differences in physical properties, in the density and refractive index.

A rather simple explanation to account for the relatively low density of the primary tar phenols occurs to the authors. This consists, in brief, in the supposition that in each group of phenol homologs the isomers which predominate in the low-temperature tar acids are those having the alkyl side chains meta or para to each other, while in the high-temperature tar acids an ortho grouping of the same alkyl chains predominates. Examination in the literature of the only group of aromatic homologs for which fairly complete density figures are available, the polymethylated benzenes, reveals rather strikingly the effect of the ortho grouping of side chains in elevating the densities, as shown in Table III, taken from International Critical Tables, and in Figure 3.

Table III. Density Figures

Hydrocarbon	Boiling Point ° C.	d_4^{20}	n_D^{20}
Benzene	80	0.878	1.5014
Toluene	110	0.866	1.4962
o-Xylene	144	0.879	1.5058
m-Xylene	139	0.865	1.4973
p-Xylene	138	0.861	1.4956
1,2,3,-trimethylbenzene	176.5	0.895	1.5132
1,2,4-trimethylbenzene	170	0.870	1.5051
1,3,5-trimethylbenzene	165	0.863	1.4967
1,2,3,4-tetramethylbenzene	204	0.901	1.5187
1,2,3,5-tetramethylbenzene	197	0.894	....
1,2,4,5-tetramethylbenzene	193	0.888	....

It is worthy of note in this connection that the largest 0.5° fraction that was obtained in the fractionation of the low-temperature tar phenols, that boiling from 234° to 234.5° C., was found to consist largely of 3-methyl-5-ethylphenol—i. e., the alkyl groups were in a meta position to one another, while the phenol of $C_9H_{12}O$ formula which was isolated from the 218° to 220° C. fraction was mesitol, in which the three methyl groups are again in a meta grouping.

Of course, the above evidence is entirely too fragmentary to make the proposition anything more than mere conjecture, nor are there sufficient data on the pyrolytic behavior of these phenols to enable one to predict whether the homologs with the alkyl side chains in ortho position to each other would be more stable and hence would be likely to remain in high-temperature tar, whereas the others would be, to a greater extent, destroyed. It is hoped, however, that future workers in this field may devote further attention to this question, and it is suggested that the fractional liberation of the phenols from their phenolate solutions, together with the oxidation of their ethers, offers a convenient method of separating and identifying the isomers.

FRACTIONATION OF TAR ACIDS

The fractionating column used was 1.65 meters long, 12 mm. internal diameter, and packed with 5 × 5 mm. glass Raschig rings. It was connected to the flask by a ground-glass joint and the whole apparatus was made of Pyrex glass. An air condenser or dephlegmator at the top of the column maintained an adequate reflux ratio (approximately 15 to 1). To prevent heat loss the column was surrounded by a closefitting concentric glass tube wound with nichrome ribbon which was heated electrically, and the whole assembly was jacketed to avoid drafts.

From the tar acids which had been distilled on a larger scale under reduced pressure, two large fractions were collected over the ranges 225° to 240° C. and 240° to 255° C. These were each separately fractionated at atmospheric pressure, cuts being taken at progressively smaller intervals. The results for the sixth fractionation of acids boiling 225° to 240° C. are shown in Figure 2. The largest fraction, boiling at 234° C., was selected for particular examination. The fractionation of acids of boiling range 240° to 255° C. was not carried beyond the fifth distillation (Figure 2).

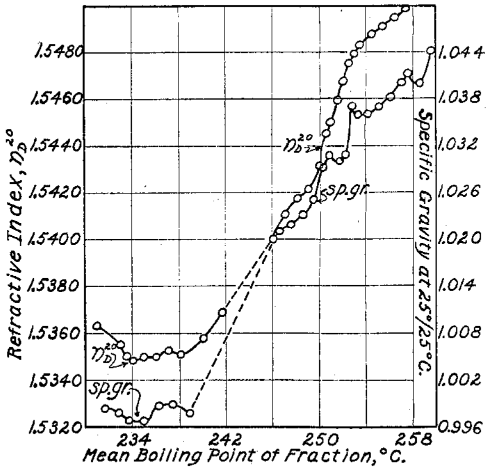


Figure 2. Refractive Index and Specific Gravity of Fractions after Last Fractionation

Fraction 220° to 225° C.

Methylation. Samples of the 5° C. cuts obtained after the third distillation of the xylenol range of tar acids were dissolved in an excess of 10 per cent sodium hydroxide solution and converted to their methyl ethers by treatment with dimethyl sulfate. Molecular weights of the ethers were then obtained by the cryoscopic method in benzene.

Table IV. Molecular Weights

Fraction ° C.	Molecular Weight of Phenol
205–215	126
215–220	131
220–225	130
225–230	141
230–235	143
235–240	149

Separation by Fractional Liberation from Phenolates. A sample of 185 grams of phenols boiling from 220° to 225° C. was dissolved in the equivalent amount, 500 cc., of 10 per cent caustic soda solution. This alkaline solution was twice treated with 50 cc. of ether, shaking thoroughly in a separatory funnel for each extraction (extract 1). Then 65 cc. of 2.5 *N* hydrochloric acid were added, 15 cc. at a time, shaking after each addition. The precipitated phenol was extracted with 100 cc. of ether. Another 65-cc. portion of the acid was similarly added, followed by shaking with ether, etc. In all, 500 cc. of acid were added, making 8 extractions. The ethereal extracts were washed with dilute acid, then with water, and after drying over anhydrous sodium sulfate the ether was removed on the water bath. The phenol portions were distilled at 15 mm. pressure.

Table V shows the degree of separation of compounds that was obtained.

The molecular weights were determined by the cryoscopic method, using the methyl ether of the phenol with benzene as solvent. Of known phenols of molecular weight 136 boiling within the range 215° to 225° C. the following are described: mesitol (2,4,6-trimethylphenol), boiling point 220° C.; 2-methyl-5-ethylphenol, boiling point 220° C.; and 2-ethyl-5-methylphenol, boiling point 226° C.

Mesitol, being substituted in both ortho positions to the hydroxyl group, would be less acid than the xylenols present and therefore would be expected in the first fractions. Fraction 1 was therefore redistilled at atmospheric pressure and that part boiling between 218° and 220° C. was taken for examination.

Bromides. A portion (5 grams) of the phenols boiling at 218° to 220° C. was brominated in the cold, in chloroform solution, by addition of one molecular equivalent of bromine. The monobromide was distilled under reduced pressure after removal of the solvent. Since no solid product could be obtained, a second molecule of bromine was added. On cooling, a crystalline solid (4 grams) separated from the chloroform solution. After recrystallization it had a melting point of 159° to 160° C. Analysis showed this to be a dibromide, $C_9H_{10}OBr_2$.

Calculated for $C_9H_{10}OBr_2$: Br, 54.33. Found: Br, 54.2.

Dibromomesitol is described as having a melting point of 159° to 160° C. The melting point of a mixture of the above dibromide with an authentic specimen of 3,5-dibromomesitol was unchanged. In this way the identity of the above dibromide was established and the presence of mesitol in the tar acids boiling at 220° C. confirmed. The residual liquid bromide was not examined further.

Table V. Separation of Compounds

Fraction	Weight *Grams*	n_D^{20}	Molecular Weight
1	35	1.5335	133.5
2	25	1.5350	132
3	25	1.5350	134
4	25	1.5360	129
5	25	1.5360	127
6	20	1.5360	127
7	20	1.5380	126
8	10	1.5380	125

Methyl Ether. The methyl ether of the phenol boiling at 218° to 220° C. was prepared by treatment at 30° C. of an alkaline solution of the phenol with dimethyl sulfate. This ether had a boiling point of 203° C., and molecular weight of 147 by the cryoscopic method in benzene. $C_9H_{11}OCH_3$ requires a molecular weight of 150.

Fraction 234 0° to 234.5° C.

This was the largest 0.5° cut obtained after the sixth fractionation of the original fraction, 225° to 240° C.

Calculated for $C_9H_{12}O$: C, 79.4; H, 8.82. Found: C, 79.98; H, 9.00.

Phenylurethan. The method found to be best applicable for the preparation of the phenylurethan of this phenol fraction was that described by Wehuizen *(10)*, who recommended carrying out the reaction in petroleum naphtha (boiling point, 170° to 200° C.) solution, obtained for this work by the fractional distillation of some commercial kerosene. Three grams of the tar acid, 3 grams of phenyl isocyanate (a slight excess over molecular equivalent), and 7 cc. of the petroleum naphtha (170° to 200° C.) were mixed and heated on the water bath for 1 hour.

$$C_6H_5N{:}CO + C_9H_{11}.OH \longrightarrow C_6H_5NH.COOC_9H_{11}$$

After the mixture had been standing at room temperature overnight, the phenylurethan crystallized out. The yield of crude urethan was 2.1 grams, or 36 per cent of the theoretical yield. It was purified by several crystallizations from carbon tetrachloride followed by one from ligroin (80° to 100° C.). The melting point was 145° C.

Calculated for $C_{16}H_{17}O_2N$: C, 75.29; H, 6.65; N, 5.49. Found: C, 75.26; H, 6.79; N, 5.63.
Molecular weight, calculated: 255. Found (Rast's camphor method): 249.

NAPHTHYLURETHAN. This was prepared in the same manner as the phenylurethan except that α-naphthyl isocyanate was used. This reagent had the disadvantage of producing dinaphthyl urea which was insoluble in the petroleum ether and had to be separated by fractional crystallization. The melting point of the naphthylurethan was 140° C.

Calculated for $C_{20}H_{19}O_2N$: C, 78.68; H, 6.22; N, 4.59. Found: C, 78.89; H, 6.47; N, 4.59.
Molecular weight, calculated: 305. Found (in camphor): 297.

BROMIDES. Bromides of the phenol fraction were prepared by the slow addition of a chloroform solution of bromine to the phenol, also in chloroform, while cooling with ice water. After standing until the solution was only slightly colored with bromine, the chloroform was removed by a vacuum pump and the liquid residue distilled. The distillate thus obtained crystallized on cooling. By fractional crystallization from petroleum ether (40° to 60° C.) two solid bromides were obtained. A dibromide, which was the more soluble in the petroleum ether, was secured in the form of stout needles and boiled at 160° C. at 5 mm. The melting point was 150° C. A tribromide was obtained (from petroleum ether) as fine needles, melting point 91° C.

Calculated for $C_9H_9OBr_3$: Br, 64.31. Found: Br, 64.00.

A liquid, apparently a monobromide, was also obtained. On treatment with more bromine it yielded a mixture of the above two bromides.

METHYL ETHER. This was prepared by treating the sodium salt of the phenol fraction in alkaline solution with dimethyl sulfate at 40° to 50° C. The yield was almost theoretical. In benzene solution it gave excellent results for the determination of molecular weight by the cryoscopic method, unlike the phenols themselves which are highly associated in benzene.

This ether was a colorless liquid of pleasant odor and did not darken on standing. It had a boiling point of 83° to 85° C. at 12 mm.

Molecular weight, calculated for $C_9H_{12}O + CH_2$: 150. Found: 150.

OXIDATION OF ETHER. The ether was suspended in a small amount of 5 per cent sodium hydroxide solution, and boiling 5 per cent potassium permanganate solution was run in dropwise with vigorous stirring, while the reaction liquid was kept boiling. Sufficient permanganate was added to oxidize all side chains to carboxyl groups, but apparently because of side reactions, much more than theoretical was required to get a fair yield of acid. The methoxy acids when formed were quite stable. Addition of 1 liter of the potassium permanganate solution usually required 2 to 3 hours. The supernatant liquid was then generally colorless. Unchanged ether was removed by steam distillation and the solution then separated from the manganese dioxide by filtration. The manganese dioxide was twice treated with 5 per cent sodium hydroxide solution and the washings were added to the main filtrate which was then evaporated to small bulk on the water bath. On acidifying the cold concentrated aqueous solution, the organic acid was liberated and filtered off. The aqueous liquor was shaken with ether to recover the last traces of the acid product of oxidation. This gave a total yield of 43 per cent of the theoretical of crude acid which was recrystallized from acetone and benzene as flat prisms, or from water as very fine needles, melting point 275° C.

Calculated for $C_6H_3(OCH_3)(COOH)_2$: C, 55.09; H, 4.11; OCH_3, 15.81. Found: C, 55.39, 55.27: H, 4.12, 4.20; OCH_3, 15.85, 15.73.

A smaller amount of an acid, melting point 238° C., was also isolated in this oxidation and was shown to be identical with the acid obtained on the oxidation of the ether of tar acid fraction 250° to 251° C. No other acids were isolated. A small amount of sirupy residue on further oxidation gave the acid of melting point 275° C.

SYNTHESIS OF 5-METHOXY-1,3-DICARBOXYBENZENE. The starting material for this synthesis was a sample of 150 grams of 4-amino-1,3-dimethylbenzene obtained from the Eastman Kodak Company. In brief, the steps consisted of a nitration of the acetylated amine for introduction of the nitro group into the 5-position, diazotization of the amino group and replacement with H, reduction of the nitro group to the amino, diazotization of the latter, and conversion to the hydroxyl. (Since the completion of this work, the 5-amino-1,3-dimethylbenzene has been made available by the Eastman Kodak Company, greatly simplifying the above operations.) The yield of the 5-hydroxy-1,3-dimethylbenzene was only 5 grams, or 3.3 per cent of the theoretical after all these operations. This product was then methylated and oxidized with alkaline permanganate as described above. After several crystallizations from 15 per cent alcohol, the dicarboxy acid was obtained as fine needles with a melting point of 275° C. The melting point of the methoxydicarboxybenzene obtained from the tar acid fraction boiling at 234.5° C. had a melting point of 275° C. and a mixed melting point of the two was 274° C.

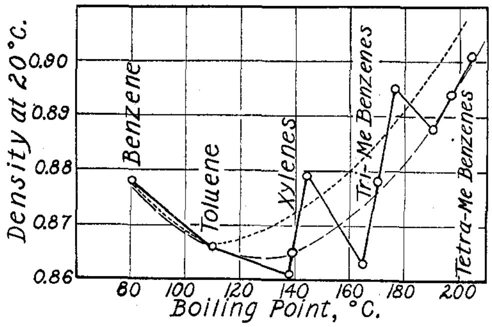


FIGURE 3. DENSITIES OF BENZENE HOMOLOGS, WITH TWO HYPOTHETICAL CURVES

Upper curve, mixture rich in ortho homologs
Lower curve, mixture poor in ortho homologs

FRACTION 250.5° TO 251° C.

This was the largest 0.5° cut obtained after the fifth distillation of the original fraction 240° to 255° C. The analyses for carbon and hydrogen content of the phenol as well as of the phenylurethan suggested a mixture of phenols, $C_9H_{12}O$ and $C_{10}H_{14}O$. No solid bromides could be obtained from this fraction of phenols.

METHYL ETHER. This was prepared as described above and gave a liquid boiling at 96° to 98° C. at 12 mm., with a pleasant odor and slightly yellow color which did not darken on standing. The molecular weight, calculated for $C_{10}H_{14}O + CH_2$ was 164; found (in benzene), 158. This suggests that this fraction is probably a mixture of phenols $C_9H_{12}O$ and $C_{10}H_{14}O$.

SUMMARY

Low-temperature tar phenols over the range 220° to 260° C. have been carefully fractionated and examined, and the fraction boiling around 220° C. shown to contain mesitol. The fraction of minimum density, boiling at 234° C., has been shown to consist mainly of 3-methyl-5-ethylphenol.

Crystalline derivatives, bromides, and phenylurethans of mesitol and methylethylphenol are described.

Examination of the fractions of tar acids up to 260° C. has indicated that they consist of mixtures of the simple alkylated homologs of phenol.

A tentative explanation for the uniformly lower densities of fractions of low-temperature tar acids as compared with

corresponding fractions of high-temperature tar acids is offered.

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Short-Cut Method of Hydrocarbon Analysis

II. Application to Analysis of Stabilizer Bottoms

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A short-cut method of hydrocarbon analysis applicable to certain types of routine samples has been developed to reduce the time and expense of such analyses. Its application to the analysis of stabilizer gas and reflux has previously been described, and its further application to stabilizer bottoms is described in this paper.

Synthetic samples, covering the range of compositions normally found for stabilizer bottoms, have been made up and run by the short-cut method employing the changes in apparatus and procedure necessary for samples of this type. From the resulting distillation curves, graphs have been prepared by the use of which routine samples of stabilizer bottoms may be analyzed. In the use of these graphs, corrections must be applied for the presence in such samples of certain constituents not present in the synthetic samples, and correction charts for this purpose have been prepared by calculating the effect of these components on the distillation curves.

This method, applied to stabilizer bottoms, checks microfractionation analysis within 0.5 per cent on the propane, 1 per cent on the butane, and 2 per cent on the pentane and hexane plus heavier hydrocarbon fractions. It offers distinct advantages from the standpoint of ease of operation and economy in time and materials.

IN VIEW of the fact that control of refinery equipment requires frequent analyses of samples of similar composition, it was felt that a rapid, economical, and accurate method of analysis would be of great value. Such a method, based on a distillation analogous to the Engler distillation for naphthas, was described by Rosen and Robertson (*7*) and is now being used by several laboratories for analyzing stabilizer gas and reflux. In the present paper its application to the analysis of stabilizer bottoms is described.

So-called graphic methods of analysis are limited in application because they are based on physical characteristics of the mixture to be analyzed, and the number of components which can be determined is only one more than the number of determinable physical characteristics. In the short-cut method the analysis is obtained by considering temperatures at different per cents-off on a distillation curve. Thus, for three-component mixtures or mixtures which can be reduced to three components, such as stabilizer gas and reflux, it is necessary to consider temperatures at two different per cents-off, while for four-component systems, or mixtures which can be so treated, such as stabilizer bottoms, it is necessary to employ temperatures at three different per cents-off.

Several graphical methods for the analysis of hydrocarbons and similar mixtures have been described in the literature. Colman and Yoeman (*4*) supplied this principle to the analysis of mixtures of benzene, toluene, and xylene. Methods for the graphical analysis of gasolines and natural gasolines from the A. S. T. M. distillation curve have been described by Smith (*8*), Pocock and Blair (*6*), and Blair and Alden (*1*), and appear to have considerable application for such hydrocarbon mixtures.

Stabilizer bottoms or similar light naphthas consist of propane, butane, pentane, and hexane plus heavier hydrocarbons having compositions varying between the two following extreme type analyses:

TABLE I. WEIGHT PER CENT OF STABILIZER BOTTOMS

SAMPLE	PROPANE	BUTANE	PENTANE	HEXANE PLUS HEAVIER HYDROCARBONS
1	3	42	45	10
2	0	22	24	54

The analysis of samples of this type by the short-cut method necessitated changes in apparatus, changes in procedure, and preparation of curves applicable to the analysis of four-component mixtures covering the above composition range. The method of attack was to develop an apparatus and procedure applicable to this type of sample, to make up synthetic mixtures representing various concentrations of the different components, to run these mixtures by the apparatus, and to prepare the graphical analysis curves from the distillation curves thus obtained.

The propane and butane used in this investigation were the same purified hydrocarbons used in the investigations by