

THE COMPOSITION OF HIGH TEMPERATURE COKE OVEN TARS

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Introduction

Until 1882 crude gas works tar was the only type produced in Great Britain since, up to that time, coking plants were not equipped for the recovery of by-products. The by-product coke oven was first developed in France and introduced at about the same time in Germany, Belgium and England. Its use, coupled with the oil washing process for benzole recovery which was introduced by Carvès in 1884, was extensively adopted in Continental Europe but it took twenty years for the advantages of by-product coke ovens to be appreciated in England. Since then, however, coke oven tar production has increased year by year reaching a peak in 1957 of 1,250,000 tons. For those interested in statistics the following table shows the production of coke oven tar in the United Kingdom in the years 1950 - 1960.

Table 1  
Production of Coke Oven Tar in the U.K. 1950 - 1960

Year	Tonnage Produced	% of all Tar Produced
1950	931,127	35.55
1951	977,379	35.64
1952	1,032,361	36.22
1953	1,056,767	37.10
1954	1,095,085	37.37
1955	1,101,294	36.76
1956	1,191,129	38.33
1957	1,252,079	40.27
1958	1,164,554	40.03
1959	1,096,399	40.40
1960	1,187,205	42.42

About 150,000 tons of crude coke oven tar is burned, the remainder is distilled for the manufacture of pitch, creosote, naphthalene, anthracene, some benzene, toluene, xylenes and naphthas and phenol and cresylic acid. It will be noted that coke oven tar accounts for about two-fifths of the total tar production in the U.K. The remainder in 1960 was made up of continuous vertical retort tar (42.85%), intermittent vertical retort tar (4.05), horizontal retort tar (5.42%), low-temperature tar (2.08%) and other types (1.17%).

Coke oven tar thus represents an important raw material whose chemical composition has been the subject of considerable study during the past sixty years. To date some 400 individual components have been isolated or identified and it is probably safe to say that at least that number are still unidentified. The vast majority of the components are present in very small amounts and can never be of any commercial interest. It is not the intention in this paper to recite a catalogue of the known components of high-temperature tars; many exhaustive compilations exist, one of the most comprehensive and complete being that compiled by K.C. Linepensel of Koppers Co. Inc.

#### Assays of Coke Oven Tars

Until recently, published analyses of coke oven tars took the form of distilling the crude tar under rather empirical conditions into arbitrary fractions which were intended to simulate the fractions obtained on commercial practice. Frequently these fractions were given non-specific names like "light naphtha", "light creosote", "carbolic oil" etc. and the content of major components such as naphthalene or phenol recorded were not those actually occurring in the crude tar but the amounts of the component (frequently impure) which crystallized from, or could be extracted from, one of these fractions. Since the distillation conditions and the degree of fractionation, the boiling ranges of the distillate oils and the method of analysis of these oils for individual components differed for each worker, it is impossible to compare the results of most of the published assays of coke oven tars and they contribute comparatively little to our knowledge of its actual chemical composition.

A few assays of coke oven tars which determine the actual amounts of commercially important components present have been published, for example the examination of American coke oven tar by Weiss and Downs<sup>1</sup> and of Australian coke oven tars by workers at the Coal Research Section of the Commonwealth Scientific and Industrial Research Organisation.<sup>2</sup> Assays of this type on a representative selection of U.K. coke oven tars have been carried out by The Coal Tar Research Association during the past eight years and it is these which are described and discussed in greater detail below.

#### The C,T,R,A. Assay Method

Preliminary work showed that the first stage of the method could be either accomplished by solvent extraction or by distillation without altering the yields of products except the pitch yield and the amount of tar acids and tar bases. It was shown that about one third of the tar acids are retained as complexes with tar bases in the residue on solvent extraction and are not

subsequently determined in the extract. Distillation was therefore chosen as the preliminary fractionation procedure and the conditions selected were those which, by trial and error, gave the same yield of medium soft pitch (70°C K & S) as was obtained from the same tar on continuous distillation in a Wilton pipe still.

5.5 kilos of the crude tar are placed in a cast iron pot and heated gently to 200°C to remove water and light oils. The latter are then fractionated on a 30 plate low hold-up column to give benzole (up to 100°C), toluole (100-125°C) and xylole (125-150°C). The residue from this distillation is added back to the dehydrated tar in the pot still and distillation continued at a rate of 14 g./minute until the vapour temperature reaches 358°C.

The oils from this primary separation step are then washed with alkali and acid to recover tar acids and tar bases respectively and the neutral oils fractionated on a 50 plate column at progressively reduced pressure to yield seven fractions and a residue as follows:-

Fraction 1	Naphtha fraction	Boiling Range	150°C/760mm. - 137°C/100 mm.
Fraction 2	Crude Naphthalene fraction	" "	137°C/100mm. - 145°C/100 mm.
Fraction 3	Methyl Naphthalene Oil	" "	145°C/100mm. - 155°C/50 mm.
Fraction 4	Diphenyl Oil fraction	" "	155°C/50mm. - 168°C/50 mm.
Fraction 5	Acenaphthene Oil fraction	" "	168°C/50mm. - 184°C/50 mm.
Fraction 6	Fluorene Oil fraction	" "	184°C/50mm. - 150°C/20 mm.
Fraction 7	Anthracene Oil fraction	" "	150°C/20mm. - 200°C/5 mm.
Fraction 8	Heavy Oil Residue		

Each of these fractions is then analysed by suitable chemical, spectroscopic and/or chromatographic methods for the quantitative determination of its major components.

The extracted tar acids are also subjected to high efficiency fractionation and the individual fractions analysed by gas-chromatography for phenol, cresol isomers and xylenols.

The practical details of this method have been published<sup>3</sup> and are not given here.

#### The Results of Assays of British Coke Oven Tars

For the purpose of this paper it will be sufficient to set down the highest, lowest and mean values obtained for the content of major constituents in British coke oven tars. This is done in Table 2. For comparison the corresponding figures for some Canadian coke oven tars (average of 6) and one Australian coke oven tar carried out by the C.T.R.A. method are included.

Table 2

Amount of Components in British, Canadian and Australian Coke Oven Tars  
(Results are given as wt. % on dry tar)

Source	British			Canadian			Australian
	Max.	Min.	Mean	Max.	Min.	Mean	
Benzene	0.42	0.124	0.252	0.297	trace	0.119	trace
Toluene	0.353	0.090	0.224	0.467	0.008	0.148	0.14
o-Xylene	0.071	0.020	0.037	0.133	0.005	0.038	} 0.15
m-Xylene	0.175	0.056	0.106	0.215	0.009	0.069	
p-Xylene	0.072	0.020	0.040	0.083	0.003	0.026	
Ethyl Benzene	0.05	0.005	0.02	0.04	0.01	0.02	
Styrene	0.067	0.020	0.038	0.046	0.008	0.020	
Phenol	1.15	0.14	0.57	0.98	trace	0.61	1.03
o-Cresol	0.84	0.10	0.32	0.51	trace	0.25	0.28
m-Cresol	1.00	0.16	0.45	0.84	trace	0.45	0.49
p-Cresol	0.70	0.07	0.27	0.52	trace	0.27	0.25
Xylenols	1.30	0.13	0.48	0.85	0.01	0.36	0.34
High-Boiling Tar Acids	2.09	0.31	0.91	1.51	0.14	0.83	0.45
Naphtha	2.66	0.52	1.18	2.21	0.15	0.97	1.03
Naphthalene	11.31	7.29	8.94	15.30	3.08	8.80	9.44
α-Methyl Naphthalene	0.86	0.60	0.72	1.08	0.37	0.65	0.58
β-Methyl Naphthalene	1.63	1.15	1.32	1.76	0.65	1.23	1.16
Acenaphthene	1.28	0.42	0.96	1.27	0.71	1.06	-
Fluorene	1.80	0.46	0.88	1.29	0.47	0.84	1.90
Diphenylene Oxide	2.00	1.40	1.50	-	-	-	1.00
Anthracene	1.38	0.52	1.00	1.01	0.47	0.75	0.68
Phenanthrene	8.8	2.3	6.3	3.00	2.14	2.66	2.32
Carbazole	1.73	0.58	1.33	1.23	0.32	0.60	0.35
Tar Bases	2.60	1.25	1.77	2.90	1.68	2.05	1.34
Pitch (70°C K & S)	63.9	49.5	59.8	70.85	52.4	63.5	62.4

The immediately striking feature of these figures is the variation they show in the content of particular components. Thus the content of phenol and cresols found in British coke oven tars can vary by a factor of ten; naphthalene content can be as high as 11% or as low as 7% and the amount of pitch produced on distillation may be less than 50% or greater than 60%.

The reasons for these variations in the amounts of individual components in coke oven tars are not at present well defined. Qualitatively it may be said that the nature of the coal, the design of coke oven, the carbonisation conditions used and the nature of the recovery system at the carbonising

plant all play a part. The generally higher level of phenanthrene and carbazole in British tars compared with the Canadian tars or the Australian tars is almost certainly to be attributed to differences in the coal structure. Certain British and Canadian tars, which show a low content of components boiling up to 230°C (benzene, toluene, xylenes, naphthas, naphthalene and phenol), are products of plants which operate their by-product recovery system in such a way that more of the volatile carbonisation products are scrubbed from the gas and less precipitated as tar. Generally speaking high naphthalene content, high pitch yield and low tar acid content go hand-in-hand, except for tars produced from low volatile coals e.g. Welsh steam coals. These are characterized by a high naphthalene and phenanthrene content but a low pitch yield.

It may be noted in passing that the tars produced in continuous gas-works vertical retorts are much more uniform in composition.

The large variations in the content of valuable components which can occur in coke oven tars is of more than theoretical significance. To the operator of coke ovens tar is tar, an unwanted by-product which he seeks to get rid of in any way he can. But to the tar distiller it is the raw material which must be transformed into products which can be sold at a profit. Changes in operation or in the blend of coal carbonised may occur at coke ovens which affect the nature of the tar produced. The first indication which the distiller has of these changes is when his fractionating column is thrown out of balance or when his naphthalene or tar acid production mysteriously drops. His first reaction is to suspect that his distillation and recovery plant have fallen in efficiency and he frequently spends some frustrating days - or even weeks or months - trying to locate non-existent faults.

These considerations suggested that there was a real need for some simple and rapid method of analysis and characterization of tars by which the tar distiller could check whether any major variation in his raw material had occurred.

#### Characterization of Tars

With this object in view a study of all tars in the storage tanks of British tar distillers was carried out some time ago. The idea behind this study was to analyse these tars by simple and, as far as possible, rapid methods and to see, by a statistical analysis of the results, which properties showed some correlation. It was hoped that, by selecting a few key properties with which other properties are correlated, some suitable characterization index could be derived.

In all 61 tars, of which 21 were from coke oven installations, were received and the analysis method, which has been described in detail,<sup>4</sup> consisted in dehydrating the crude tar, determining the specific gravity and solvent analysis of the dry tar which was then subjected to a standard distillation to yield three distillate oil fractions, - 0-250°C, 250-300°C and 300°C - pitch and a 70 ± 2°C (K & S) residue. The distillate oils were analysed for tar acid content,

paraffin content and naphthalene content and the pitch was analysed for C/H ratio and subjected to a Mallison solvent analysis for its content of H- and M-resins.

Statistical analysis of all the results showed that the most useful index was the specific gravity of the dry tar. This gave a high degree of correlation with the pitch yield (in fact this relationship was used to determine the end point of the distillation to leave a pitch of the desired softening point) (Fig.1); it also showed a good correlation with the viscosity of the dry tar (Fig.2) and with the C/H ratio of the pitch. For the full range of tars (coke oven tars, continuous vertical retort tars, intermittent vertical retort tars, horizontal retort tars and blended tars) the correlation coefficients between specific gravity of the tar and paraffin content, specific gravity of the tar and phenol content and between phenol content and naphthalene content were statistically significant but, if the analysis was confined to coke oven tars, these correlations and that between the paraffins and tar acids or those between any of these properties and the naphthalene content were not significant as will be appreciated from the almost random distribution of points in Figures 3 and 4.

Although a characterization index was suggested based on three numbers indicating the level of dry tar gravity, phenol content of the 0-250°C distillate and the benzene insoluble content of the dry tar, this index is not of particular value in detecting changes in coke oven tar supplies to a distillery. It has proved of value in detecting changes in gas works carbonising practice and in anticipating changes in plant operation when the ratio of different types of tar in a blended feedstock is altered but it must be admitted that the problem of a simple characterization procedure for coke oven tars is still unsolved. The variations in properties of the coke oven samples examined are indicated in Table 2. This gives the maximum, minimum and mean values for the properties determined and also lists those properties for the coke oven tars with the highest and lowest phenol, paraffin and naphthalene contents (tars A1, A2, B1, B2, C1 and C2).

Table 2

Property	All Coke Oven Tars			Tar A1	Tar A2	Tar B1	Tar B2	Tar C1	Tar C2
	Max.	Min.	Mean						
Sp.Gr. of Dry Tar at 20°C	1.218	1.141	1.188	1.141	1.209	1.184	1.203	1.185	1.217
Viscosity of Dry Tar (Redwood No.1 secs at 60°C)	1.971	172	723	253	1247	382	546	438	1971
Wt.% Oils to 250°C	15.6	6.7	12.1	15.2	8.0	14.7	10.0	13.5	7.8
Wt.% Oils 250-300°C	12.2	9.3	11.30	12.2	9.4	9.7	9.7	12.2	9.6
Wt.% Pitch	69.2	52.2	61.0	52.2	66.8	59.3	62.9	59.1	68.6
% Phenols in Oil to 250°C	19.7	nil	7.8	19.7	nil	6.2	nil	9.2	9.5
% Paraffins " " "	2.3	nil	0.9	2.1	0.2	2.3	nil	1.8	0.8
% Naphthalene in Dry Tar	10.5	6.4	9.1	6.8	8.4	9.1	9.9	10.5	6.4
% Benzene Insols in Dry Tar	12.1	4.1	8.5	4.3	9.4	7.4	11.3	11.8	10.0

#### The Chemical Composition of Coke Oven Tar Distillate Oils

It is only recently, with the development of vapour chromatography, that it has been possible to obtain any information on the quantitative composition of tar distillate oils. The data so far obtained are, however, scanty and incomplete, mainly due to the limited number of reference compounds available for calibration of chromatographic columns.

#### Benzoles and Naphthas

Coke oven tar oils boiling up to 150°C which have been washed free from tar bases are remarkably uniform in composition. Their major components are benzene, 33-40%; toluene, 24-33%; m-xylene, 10-15%; o-xylene, p-xylene and styrene, about 5% each, ethyl benzene about 2% and thiophene and methyl thiophenes 1-2%. Non-aromatics which may occur in amounts up to 5%, are mainly methyl cyclohexane.

In the naphtha range (150-200°C) the main neutral components are indene, hydriindene, coumarone and pseudocumene with smaller amounts of ethyl toluene, mesitylene and hemimellitene and an amount of paraffins varying from a trace to 5%. In some samples n-propyl benzene is detectable and there is generally up to 15% naphthalene and some methyl naphthalenes depending on the efficiency of the fractionation procedure. The ratio of the components boiling up to 200°C varies considerably as is shown in Table 3 which lists the maximum, minimum and mean values.

Table 3

Composition of Coke Oven Coal Tar Naphthas (150-200°C boiling range)

Component	Wt. %		
	Max.	Min.	Mean
n-Propyl Benzene meta & para ethyl Toluenes	3.9	nil	0.6
Mesitylene	8.5	0.4	2.8
Pseudocumene	6.5	0.8	3.2
Hemimellitene	14.8	3.7	8.7
Hydrindene	6.9	trace	2.9
Indene	46.5	12.7	28.9
Coumarone	53.0	10.0	38.2
Paraffins	15.9	5.2	11.0
	10.0	nil	3.7

Naphthalene Oils

By far the major component of the tar-acid free coke oven oils boiling in the range 200-250°C is naphthalene which in well fractionated samples may be 65% of the tar-acid free oil. The remaining 35-50% is made up of thionaphthene 2-3%,  $\alpha$ -methyl naphthalene 6-10%,  $\beta$ -methyl naphthalene 15-20%, quinoline 2-5%, paraffins, mainly dodecane 0-2% and amounts of dimethyl naphthalenes, dimethyl hydrindenes and acenaphthene.

Oils Boiling in the 250-300°C Range

The analysis of coke oven wash oils and light creosotes which have so far been carried out indicate that in this range the main constituents are, as would be expected, acenaphthene, diphenylene oxide and fluorene and these three components account for at least 50% of the fraction. The remainder is very complex with numerous minor unidentified compounds. Diphenyl and dimethyl naphthalenes make up 10-20% of this range and some of the trimethyl naphthalenes have been identified in it.

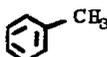
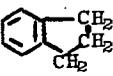
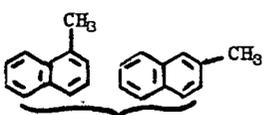
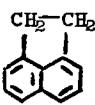
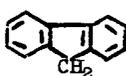
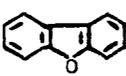
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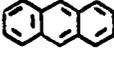
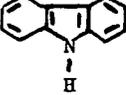
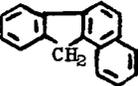
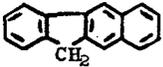
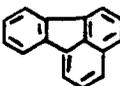
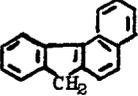
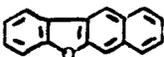
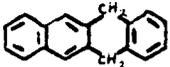
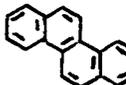
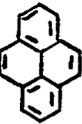
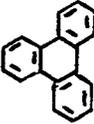
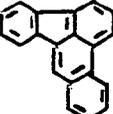
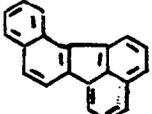
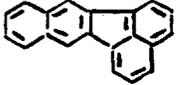
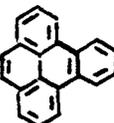
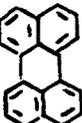
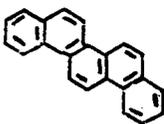
Phenanthrene, anthracene and carbazole make up on the average 75% of the coke oven tar fractions distilling from 300°C to 350°C. Phenanthrene is by far the major component, there being 6-8 times as much phenanthrene as anthracene; carbazole content is generally somewhat higher than that of anthracene. The remaining 25% consists of a large number of minor components which include tri- and tetra-methyl naphthalenes, diphenylene sulphide, phenyl-naphthalenes, acridine, methyl fluorenes and dimethyl diphenylene oxides.

### Coke Oven Pitch

As the boiling range is ascended the complexity of coke oven tar fractions increases and their analysis becomes more difficult. Not only are the limits of volatility for fractionation reached but the value of analysis by vapour chromatography becomes increasingly limited by the lack of reference compounds. 45-55% of coke oven pitch can be separated from the remainder either by exhaustive extraction with petroleum ether or by vacuum distillation. These fractions have average molecular weights in the range 200-300 and appear to contain about one OH group per ten molecules and one  $\text{CH}_2$  or  $\text{CH}_3$  group for every three molecules. NH groups occur once in every ten molecules and =N- groups once per 8 molecules. Vapour chromatography on a high-temperature column shows the main hydrocarbon components to be fluorene, anthracene, phenanthrene, pyrene, chrysene, fluoranthene, benzfluorenes, benzfluoranthenes, benzpyrenes, perylene, benzperylene and picene.<sup>5</sup> These compounds, together with brazan, dihydronaphthacene, triphenylene are the compounds which can be isolated most readily from coke oven pitch distillates or solvent extracts.

At this stage it is worth while setting down the major hydrocarbon components of coke oven tar in order of their complexity. This gives the following picture:-

Boiling Range	Average % of Tar	Major Components			
0 - 150°C	0.8			Single 6-membered rings	
		Benzene	Toluene		
150 - 200°C	2				Fused 6,5-ring systems
		Hydrindene	Indene	Coumarone	
200-250°C	12				Fused 6,6-ring systems
		Naphthalene	Methyl Naphthalenes		
250-300°C	8				Fused 6,5,6-ring systems
		Acenaphthene	Fluorene	Diphenylene Oxide	

Boiling Range	Average % of Tar	Major Components				
300-350°C	15				Fused 6,5,6- and 6,6,6-ring systems	
		Anthracene	Phenanthrene	Carbazole		
Pitch	32					
Crystalloids		1,2-Benzfluorene	2,3-Benzfluorene		Fused 6,5,6,6-ring systems	
						
		Fluoranthene	3,4-Benzfluorene	Brazan		
						Fused 6,6,6,6-ring systems
		Dihydronaphthacene	Chrysene	Pyrene	Triphenylene	
						Fused 6,6,5,6,6-ring systems
		2,3-Benzfluoranthene	7,8-Benzfluoranthene	8,9-Benzfluoranthene		
						Fused 6,6,6,6,6-ring systems
		1,2-Benzpyrene	4,5-Benzpyrene	Perylene	Picene	
						Fused 6,6,6,6,6,6-ring systems
		1,12-Benzperylene				

It would be expected that the remaining thirty odd per cent of pitch - the resinoid, C<sub>2</sub> and C<sub>1</sub> fractions - would extend this logical sequence, the number of fused rings in the main components increasing from six to a considerably high value. There is still, however, some controversy about the molecular weight of these fractions. Values obtained at C.T.R.A. by osmotic pressure measurements and by ebullioscopic determinations in benzene and pyridine vary from 400

1200 for fractions of the resinoids with an average value of about 550 and from 1000 - 1500 for the C<sub>2</sub> fraction (i.e. the benzene insoluble-pyridine soluble fraction). Other workers have recorded much lower values. These lower values we believe to be due to the presence of low molecular weight material in the fractions analysed either due to the imprecise nature of the fractionation method adopted, or more probably, to the incomplete removal of solvent from the recovered fractions.

If the results which Wood<sup>5</sup> gives for the fractions of a coke oven pitch, separated by a precise and reproducible solvent fractionation, are accepted and subjected to statistical structural analysis in the same manner in which van Krevelen and his co-workers<sup>6,7</sup> have considered coal macerals, the conclusions are that the more complex fractions of coke oven pitch form a logical extension of the series formed by the distillate oil fractions.

In carrying out this analysis certain assumptions must be made. For example it is assumed that both  $\text{-NH-}$  (determined by potentiometric titration with perchloric acid),  $\text{>N-}$  (determined from total nitrogen content, less the  $\text{-NH-}$  groups) and  $\text{-O-}$  groups (determined by subtracting  $\text{-OH}$  groups from the total number of oxygen atoms in the average molecule) are present in ring systems. Hydrogen which cannot be accounted for as  $\text{-OH}$ ,  $\text{-NH-}$  or aromatic  $\text{-CH}$  (determined from the infra-red absorption at  $3050 \text{ cm}^{-1}$ ) are assumed to be equally divided between  $\text{CH}_2$  and  $\text{CH}_3$  groups. By van Krevelen and Chermis's<sup>6</sup> "lift out and replace principle" an equivalent hydrocarbon structure may be calculated and the aromaticity (Ar) i.e. number of "equivalent" ring carbons divided by total "equivalent" carbons calculated. The number of rings in the average molecule can be derived from the formula:-

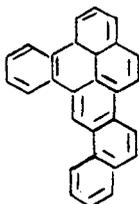
$$\text{Ar} = \left(1 - \frac{\text{H}}{\text{C}}\right) + \left[1 - \frac{2(\text{R}-1)}{\text{C}}\right]$$

and by subtracting the number of "equivalent" ring  $\text{-CH}_2-$  groups and the number of  $\text{-CH}_2-$  and  $\text{-CH}_3$  groups from the total number of "equivalent" C atoms, a figure is obtained for the number of C atoms at the junction of fused rings.

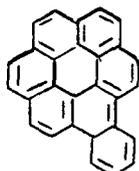
The largest fraction - that soluble in heptane-dioxan - has a molecular weight of 220, an average formula of  $\text{C}_{15.7}\text{H}_{11.7}\text{O}_{.21}\text{N}_{.22}\text{S}_{.07}$  and an "equivalent" hydrocarbon structure of  $\text{C}_{17.1}\text{H}_{12.3}$ . Its aromaticity is 0.98, the average number of rings per molecule is 3.6 and the number of ring joining carbon atoms per molecule is 5.3 which suggests an average degree of condensation similar to that found in pyrene. These results are consistent with what other data are available for the structure of pitch crystalloids.

The next major fraction which makes up 10% of the pitch is that soluble

in heptane and this has a molecular weight of 400, a molecular formula of  $C_{29.3}H_{19.5}O_{0.93}N_{0.49}S_{0.14}$ . It contains on the average 7 rings per molecule, an aromaticity of 0.923 with, on the average 2.13  $CH_2$  or  $CH_3$  and 0.19 OH groups per molecule. The number of ring-joining atoms is 11.9 which for 28.6 equivalent ring carbons ( $C_R$ ) is close to  $\frac{C_R}{2} - 3$  and consistent with a structure such as I rather than II.

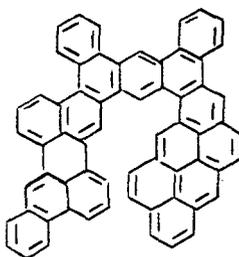


I



II

The next major fraction is that insoluble in methanol but soluble in benzene whose number average molecular weight is 910 and whose molecular formula is  $C_{83.5}H_{41.0}O_{1.49}N_{1.04}S_{0.31}$ . It has an aromaticity of 0.92 and the average number of rings in the molecule is 17.4. Ring joining carbons total 31 and the equivalent ring carbons 64.8. This again is more consistent with a "ring-chain", fairly open structure than a closely packed, highly condensed structure. Thus the seventeen ring aromatic system, III has 64 ring carbons and 32 ring joining carbons against 50 carbon atoms and 32 ring joining carbons for the highly condensed system IV.



III



IV

It is, however, only right to point out that the two smaller fractions of the pitch amounting to 1.3 and 3.4% of the pitch respectively do not fit into the series; it is, however, believed that the analytical results on these are unreliable because of adsorbed solvents.

Tar Acids

65 to 70% of the tar acids extracted from the distillate oils are made up of phenol, cresols and xylenols, the distribution being as indicated in Table 4.

Table 4Composition of Phenols Extracted from Coke Oven Oils

Tar Acid	wt. % of Total		
	Max.	Min.	Mean
Phenol	30	14.3	19.0
o-Cresol	11.3	8.7	9.8
m-Cresol	16.3	13.5	14.8
p-Cresol	9.5	7.1	8.2
Xylenols and ethyl phenols	17.6	6.4	14.1
Higher Boiling Tar Acids	36.9	28.7	34.1

The higher boiling tar acids are a complex mixture of which the major constituents are 3-methyl-5-ethyl phenol, 2-methyl-4-ethyl phenol, 4-indanol, 5-indanol, 6-methyl-4-indanol, 7-methyl-5-indanol,  $\alpha$ -naphthol and  $\beta$ -naphthol.

Tar Bases

No complete analysis of the bases extracted from the distillate oils of British coke oven tars is as yet available. According to the C.S.I.R.O. workers<sup>2</sup> the bases from an Australian coke oven tar contain 33.17% quinoline, 8.28% isoquinoline, 8.92% quinaldine, 0.91% 8-methyl quinoline and 3.21% 6-methyl quinoline.

The General Structure of Coke Oven Tars

The data given in this paper indicate that high-temperature coke oven tars are complex mixtures of aromatic and heterocyclic ring compounds. At the lower end of the boiling range single six-membered ring systems occur, with their corresponding hydroxy and alkyl substituents and the alkyl groups, while predominantly methyl, include ethyl and n-propyl side chains. Single ring compounds make up, however, less than 5% of tar. They are followed, as the boiling range is ascended, by fused six and five membered ring systems with their corresponding methyl and hydroxyl substituents; such systems, however, again make up less than 5% of the total. The next members of the ascending series - molecules containing two fused six membered rings, two six membered rings and one five membered ring, or three fused six membered rings - are major constituents making up some 30-35% of the tar. In this range naphthalene and phenanthrene are the major components with the other unsubstituted aromatic

compounds, acenaphthene, fluorene and anthracene, also prominent. Methyl and dimethyl derivatives of these aromatic hydrocarbons and the corresponding heterocyclic compounds occur as minor constituents. Oxygen compounds with the oxygen in a five membered ring are the most common heterocyclic compounds followed by tertiary bases with the nitrogen in a six membered ring system or as  $-NH-$  in a five membered ring.

The same pattern is preserved in the pitch oils which make up about 30% of the tar. These consist predominantly of unsubstituted aromatic hydrocarbons containing from four to seven or eight fused rings and, in general, the ring systems are not fully condensed. Methyl and hydroxy substituents are rare but do occur and about ten per cent of the molecules contain a heterocyclic oxygen, nitrogen or sulphur atom in the ring system in this order of abundance. Compounds containing more than one heterocyclic atom are rare and, although polyphenyl compounds are present, they are very minor components. Compounds with partly substituted ring systems are also present in small amount but in most of the compounds containing ring  $-CH_2-$  groups, the  $-CH_2-$  is part of a five membered ring.

The most complex 30% of pitch represented by the pitch resins and the so called  $C_2$  and  $C_1$  fractions appears, from our present knowledge, to be a continuation of the series formed by the less complex and more volatile fractions and consists essentially of ring compounds containing from 8 to more than 20 rings in the molecule. The evidence, however, points to the fact that these more complex constituents have ring systems which are not highly condensed but rather consist of highly branched ring chain structures in which the majority of the rings are fused to no more than three other rings.

As further evidence of the relatively low degree of condensation in the ring structure of the molecules in pitch, may be cited the fact that the infrared spectra of pitch fractions shows much stronger bands at  $750\text{ cm}^{-1}$  due to ortho substitution in the aromatic ring than at the other wave lengths characteristic of other types of substitution, indicating that there are a fair number of unsubstituted end-rings i.e. rings fused to only one other ring.<sup>5</sup>

#### The Composition of Tars and the Structure of Coal

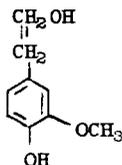
It has been said that the products of carbonisation of coal have about as much resemblance to the original coal structure as the fragments of ash from a burning library bear to the original books. On the other hand tar accounts for 15% of the coal structure in low-temperature carbonisation and, despite the complexity of the reactions occurring in the carbonisation process, some inferences as to the nature of the coal "molecule" should follow from a study of the composition of the tar.

This approach has been made by Karr and his co-workers<sup>8 9</sup> on the basis of the divergence between the determined distribution of isomers in low-temperature tars and the predicted thermodynamic and kinetic distributions at the temperature of carbonisation. Karr's argument is that the tar produced

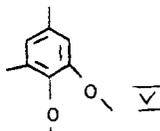
in low-temperature carbonisation of coal may be regarded either from the standpoint of thermodynamic equilibria or chemical kinetics. If thermodynamic equilibrium has been achieved the proportion of various isomers will be that predicted by theory. If the residence time is too short to enable equilibrium to be achieved the most abundant isomers should be those predicted from the relative rates of formation. Isomeric distributions outside the range predicted by the combined thermodynamic and kinetic systems might indicate dependence on the coal structure.

An examination of the distribution of alkyl benzenes, alkyl phenols, phenyl pyridines, methyl quinolines and substituted anilines found in low-temperature tars showed very considerable differences from the distributions predicted on either thermodynamic or chemical kinetic considerations. Particularly striking was the relatively high proportion of para isomers in structures for which thermodynamic equilibria predicted a preponderance of the meta isomer and kinetic consideration a preponderance of the ortho compound. There seemed, therefore, some justification for the suggestion that these isomers derived from some common monomeric unit of the coal structure. One such unit which would account for the isomeric distributions found and whose occurrence when coal is carbonised would be biogenetically plausible is 4-n-propyl-2-methoxy phenol derived from lignin which has been subjected to the coalification process.

Prior to Karr's publications a similar idea had been put forward, although not published, by W. Waddington of The Coal Tar Research Association. His suggested structure of that part of the coal molecule from which tar is derived was that of a polymer consisting of a long paraffinic or conjugated chain from which at intervals were attached 4-alkyl-2-methoxy phenol units, substituted in the 6-position by other paraffinic or conjugated side chains. It is now generally agreed that Freudenberg's view of the biosynthesis of lignin from coniferin via the condensation of monomeric units of the structure

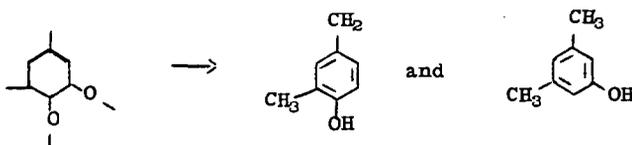


is probably correct, and although the structure of lignin has not been finally clarified, the production, on pyrolysis of fossilised lignin, of a unit having the structure V is not difficult to envisage.

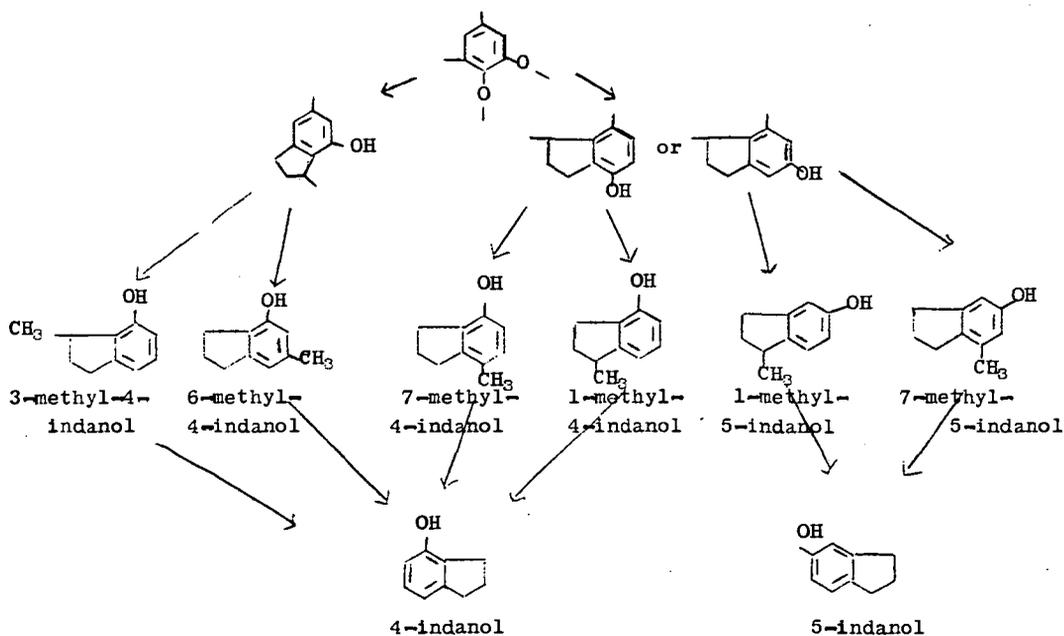


The isomeric distribution of the xylenes and cresols in high-temperature tars is as expected from thermodynamic considerations with the meta compound predominating but in the xylenols the observed distribution in continuous

vertical retort tar differs from what would be expected from either thermodynamic or kinetic considerations. Thus the observed distribution is 33% 2,4-xylenol, 31% 3,5-xylenol, 12% 2,6-xylenol and between 7-9% of each of the 2,3-, 2,5- and 3,4-isomers. The thermodynamic distribution should give almost equal amounts of the 2,4-, 2-5- and 3,5-isomers while from kinetic considerations the 2,4- and 3,4-isomers would be expected to predominate. Shortening of the side-chains and loss of one or other of the oxygen containing groups would yield 2,4-xylenol or 3,5-xylenol from the proposed coal degradation product:-

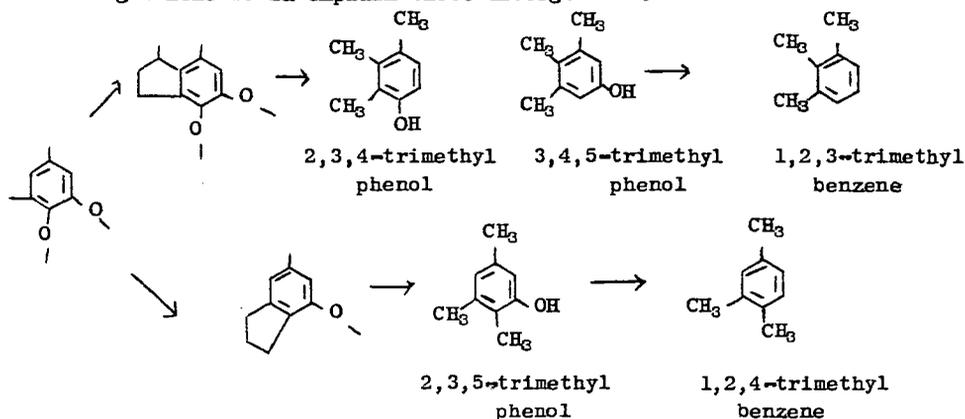


In the higher boiling tar acids from both low-temperature and high-temperature tars, 4-indanol and 5-indanol and their monomethyl derivatives predominate. These can be regarded as derived from the postulated progenitor thus:-

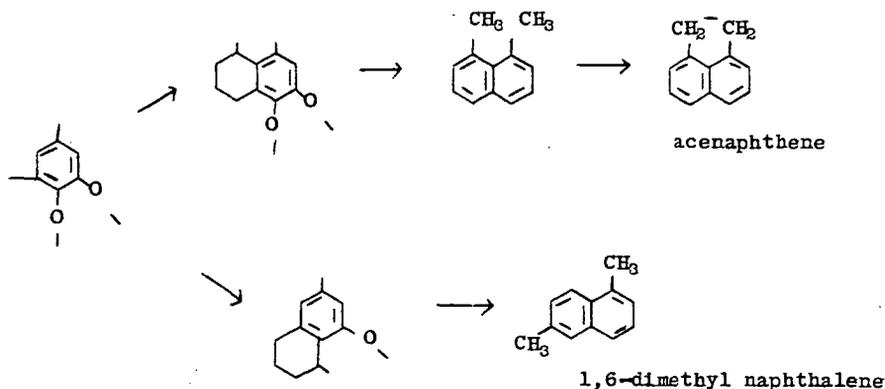


The distribution of the isomeric methyl indanols found in vertical retort tar is 18 parts 7-methyl-5-indanol: 12 parts 3-methyl-4-indanol: 8 parts each of 6-methyl-4-indanol, 7-methyl-4-indanol and 1-methyl-5-indanol: 6 parts of 3-methyl-5-indanol: 1 part each of 4-methyl-5-indanol and 6-methyl-5-indanol. It will be seen that this distribution, except for the absence of 1-methyl-4-indanol, is in conformity with the above scheme.

The trimethyl phenols found in vertical retort tars are restricted to the three isomers 2,3,4-trimethyl phenol, 2,3,5-trimethyl phenol and 3,4,5-trimethyl phenol. Also the isomeric distribution of the three trimethyl benzenes in tar is in the order 1,2,3 > 1,2,4 > 1,3,5 whereas both the thermodynamic and kinetic distributions would predict 1,2,4 > 1,3,5 > 1,2,3. The following scheme would explain these divergencies.



If ring closure yields six-membered rings the predominant products would be expected to be acenaphthene and 1,6-dimethyl naphthalene.



whereas experimental thermodynamic evidence favours the 2,6- and 2,7-isomers as the predominant forms. The analysis of the 250-300°C fractions of continuous vertical retort tar give the ratio of acenaphthene and dimethyl naphthalenes as acenaphthene 1.0, 1,6-dimethyl naphthalene 0.44, 2,6- and 2,7-dimethyl naphthalenes 0.35, 1,7-dimethyl naphthalene 0.19, 2,3-dimethyl naphthalene 0.16 and 1,5-dimethyl naphthalene 0.14.

It is appreciated that the evidence from the isomer ratios of tar components for a common precursor derived directly from the coal structure is very flimsy but it seems an interesting speculation and it is in this sense that it is mentioned in this paper. As more reliable data accumulate on the fine structure of tar fractions, particularly those from primary and low temperature tars, and better data become available, either from calculations or experiments of the thermodynamic distribution and kinetic distribution of isomers at the carbonisation temperatures, it should be possible to provide stronger evidence for or against this hypothesis. This possible approach to the problem of the chemical structure of coal should not be ignored.

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