

RECENT ADVANCES IN THE CHEMICAL CONSTITUTION OF COAL

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The problem of chemical constitution of coal has long remained an intractable one but intensive work carried within the last decade in particular has steadily revealed important information on the structural pattern of coal. Since 1952 the concept of the structural parameters has emerged and, broadly speaking, whatever has been achieved so far mainly concerns this aspect of coal structure. By structural parameters is generally meant the state of combination of carbon, hydrogen and oxygen and their distribution in the average structural 'unit'. Such knowledge has been obtained from various physical studies e.g. x-ray<sup>1-8</sup>, infra-red<sup>9-11</sup>, nuclear magnetic resonance (n.m.r.)<sup>12-14</sup>, proton spin resonance (p.s.r.)<sup>15</sup>, electron spin resonance (e.s.r.)<sup>16-18</sup> and statistical techniques<sup>19-23</sup> involving density, refraction, sound velocity, magnetic susceptibility<sup>24</sup> and other properties.

Recently a number of chemical techniques<sup>25-40</sup> have been developed in these laboratories to assess the structural parameters in coal as revealed by physical measurements. In the main, these constitute oxidation, pyrolysis, and dehydrogenation and have led to important information on the state of combination of carbon and hydrogen in coal as well as on the size of the aromatic nucleus.

AROMATIC CARBON IN COAL:

Carbon is the predominant element in coal and the major part of it is believed<sup>41</sup> to be aromatic in character.

Two chemical techniques, namely, oxidation<sup>25,28</sup> and pyrolysis<sup>31</sup>, have been employed by the authors for the quantitative measurement of the aromatic carbon. It is believed that by these methods of treatment the non-aromatic structure is preferentially oxidized or devolatilized leaving the aromatic skeleton of coal unaffected. It may as well be that the mechanisms of oxidation or pyrolysis of coal are not as simple as that. Hence, in more recent work<sup>42,43</sup> further support of the validity of the oxidation and pyrolysis techniques has been obtained by applying the methods on reduced coals. This is because in reduced coals the essential features of the original structure are believed to be retained, but the distribution of carbon and hydrogen in two forms, aromatic and non-aromatic, are altered.

A series of vitrains were reduced with lithium and ethylenediamine following the technique of I. Wender<sup>44</sup> and his co-workers. This treatment creates fresh hydroaromatic structure at the expense of the aromatics. The aromaticity of reduced coals can be theoretically calculated from the amount of hydrogen added during reduction provided that the aromaticity of the original coals as determined by chemical techniques are assumed to be correct. The aromaticity of the reduced coals as determined by oxidation as well as by pyrolysis studies have been found to be in excellent agreement with the theoretical values as reproduced<sup>42-43</sup> in Tables 1, 2.

Recent physico-chemical deductions<sup>45,46,50,66,68</sup> based on infra-red<sup>4,9</sup> and n-m-r<sup>13-14</sup> data especially those<sup>45-46</sup> put forward by the authors (Table 3) also give values of aromaticity which are in good agreement with those determined by the chemical methods of oxidation and pyrolysis (Fig.1). The values of aromaticity obtained by chemical techniques can perhaps be taken to be more precise than those deduced earlier by physical techniques.

Now that a precise estimate of aromaticity is available from chemical methods, it is of interest to compare such values with those earlier assessed by a number of physical techniques. Such comparison is depicted in Fig. 2. It is found that the values of "ordered" carbon obtained by x-ray diffraction studies<sup>3</sup> closely fall in line with the most acceptable values of aromaticity. Assessment of non-aromatic structure and hence of the aromatic by infra-red studies is rendered difficult because of the lack of precise data on extinction coefficient ratio required for computation. Thus no firm values of aromaticity could be obtained by such methods. The preferred values of aromaticity obtained by I.G.C. Dryden<sup>47</sup> by a study of the self-consistency between several physical techniques are about 5 to 10 per cent higher than those directly obtained by chemical studies and cannot be reconciled with the values of alicyclicity obtained by the authors<sup>37</sup>. The values of aromaticity deduced by any of the statistical techniques made by van Krevelen and co-workers<sup>19-23</sup> are also 10-15 per cent higher than those obtained later by chemical techniques (Fig. 1). Their values of aromaticity can also not be reconciled with the most preferred values of alicyclicity (determined in these laboratories), because the sum of the two exceeds the total carbon in coal (Table 4). If the amount of methyl carbon is taken into consideration the discrepancy would increase still further.

It will be of interest to note that the differences between values of aromaticity obtained by different techniques are greater in the case of coals of lower rank, but they tend to narrow down for higher rank coals. This may perhaps be explained by the inherent difficulties in the accurate measurement of the physical parameters owing to the possible interference by the presence of more oxygenated groups in coals of lower rank.

#### NON-AROMATIC CARBON IN COAL

##### (a) Alicyclic Combination

Information about the disposition and character of the non-aromatic carbon in coal has recently been obtained by the authors by a series of dehydrogenation studies<sup>32-40</sup>. It has been shown that the non-aromatic structure of coal is predominantly alicyclic.

The first estimates of alicyclicity<sup>32-33</sup> were obtained by employing Vesterberg's technique of dehydrogenation. The results so obtained were confirmed by another method of dehydrogenation with iodine. These estimates indicated that broadly 10-25 per cent of the carbon is in alicyclic combination in the bituminous range (carbon : 80-90 per cent). The alicyclicity progressively diminishes with increase in rank and is practically non-existent in the anthracite stage.

Subsequently, M.E. Peover<sup>48</sup> introduced the benzoquinone method of dehydrogenation and obtained much higher results. It has recently been shown by the authors<sup>37</sup> that the higher estimates of Peover may have been due to some systematic error in the polarographic determination of hydroquinone produced as a result of the dehydrogenation of coal. In fact, an investigation of the benzoquinone method in these laboratories has shown that the three methods of dehydrogenation viz. by sulphur, iodine and benzoquinone are comparable in so far as the extent of dehydrogenation possible in different ranks of coal (Table 5).

Further, the applicability of Vesterberg's technique in the dehydrogenation of coal structure has been corroborated by determination of hydroaromaticity in reduced coals. It has been found<sup>49</sup> that the freshly created hydroaromatic structure in the reduced coals undergoes dehydrogenation with sulphur quantitatively, apparently without any side reactions. These results are reproduced in Table 6.

Thus, the values of alicyclicity originally presented<sup>32-33</sup> from these

laboratories in 1958 should be treated as largely correct (Fig.3)\*. In fact, the amount of hydrogen which could be added to coal at any stage of reduction could be quantitatively removed<sup>49</sup> during dehydrogenation with sulphur (Table 6). This indicates that coal structure is perhaps unique in its chemical reactivity and that the estimates of alicyclicity obtained by treatment with sulphur are possibly the maximum values.

An immediate consequence of dehydrogenation studies has been the recognition of the fact that the sum of aromatic and alicyclic carbon appears to be virtually constant at the level of 92 per cent of the total carbon in coal, irrespective of its rank, from lignite to the highest rank bituminous coal. The same conclusion repeatedly emerged from the pyrolysis studies on dehydrogenated coals and coals pre-treated with different chemical reagents<sup>57</sup>. The aromaticity progressively increases at the expense of the alicyclic structure, with increase in rank and this appears to be the principal mechanism<sup>40</sup> involved in geo-chemical metamorphism of coal in the bituminous range. The implications of this concept has been discussed elsewhere<sup>40</sup> and has possibly led to a better understanding of the pattern of coal structure and its variation during the genesis of coal. The physico-chemical deductions later made by A.F. Gaines<sup>50</sup> as well as by the present authors<sup>45-46</sup> (Table 3) also point to this constant feature of coal structure.

#### (b) Aliphatic Combination

As the aromatic and alicyclic carbon constitute about 92 per cent of the total carbon in coal, the aliphatic carbon would amount to about 8 per cent. Attempts made by several workers<sup>51-53</sup> to estimate the methyl groups in coal by employing Kuhn-Roth reaction have indicated that hardly 3-4 per cent of the carbon is possibly present in this form. This leaves another 4 per cent of the carbon unaccounted. From certain structural considerations the present authors suggested earlier that this unaccounted carbon could also be present<sup>27,40</sup> in the form of methyl groups. It is well-known that Kuhn-Roth method cannot be applied for the quantitative determination of  $\beta$ -methyl groups linked to aromatic structure and hence estimates of  $\beta$ -methyl groups by such procedure can only be minimum values.

From recent p.s.r. measurements made by Oth & Tschamler<sup>15</sup> it appears that 30-35 per cent of hydrogen may be present as constituents of  $\beta$ -methyl groups in coal. This is consistent with the authors' view that about 8 per cent of carbon in coal is present as methyl groups. Recent physico-chemical deductions<sup>45</sup> made by the present authors also lead to a similar conclusion (Table 3).

Nevertheless, direct experimental proof for the above supposition is yet to come. In this context the question of the probable presence of angular methyl groups in coal structure cannot be disregarded in view of strong indications for the same from dehydrogenation studies<sup>33</sup>.

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\* van Krevelen et al.<sup>37</sup> had questioned the validity of Vesterberg's technique in the selective dehydrogenation of the alicyclic structure. Further studies<sup>38,39</sup> made since then indicated that side-reactions, if any, appeared to be minor and, accordingly, a revised estimate of minimum alicyclicity was presented. However in more recent studies<sup>49</sup> by the authors on reduced coals, it appears that, in so far as coal dehydrogenation is concerned, the Vesterberg's technique is possibly specific in the dehydrogenation of the alicyclic structure. A fuller account of the recent developments is being presented elsewhere<sup>49</sup>.

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### HYDROGEN IN COAL

From chemical studies attempts have also been made to determine the different forms of hydrogen in coal, aromatic, alicyclic and aliphatic. Oxidation and pyrolysis techniques have enabled measurements of hydrogen broadly in two forms - aromatic and non-aromatic. Such measurements are not in good agreement with those assessed by infra-red studies. The discrepancy between these two sets of estimates is possibly due to inherent difficulties in the measurements of optical density and its interpretation which requires precise values for the extinction coefficient ratio. The estimates of aromatic and non-aromatic hydrogen made by the authors by oxidation and pyrolysis are mutually consistent (Fig.4). Further, it has been recently shown elsewhere<sup>54</sup> that the same techniques of oxidation and pyrolysis can also be successfully employed to determine the altered distribution of hydrogen in reduced coals. It may, therefore, be concluded that the variation of hydrogen in aromatic and non-aromatic form with increase in rank as determined by chemical methods by the authors can be considered the most acceptable at the moment. Such determinations were also reported by Van Krevelen<sup>55</sup> a few months later but only by the pyrolysis technique: his results are in agreement with the authors' values and are also shown in Fig.4. Probably re-assessment of the extinction coefficient ratio in case of infra-red results may reconcile the discrepancy between the two sets of estimates, made by physical and by chemical methods. J.K. Brown et al<sup>10,11</sup> have claimed to have given support to their preferred values of extinction coefficient ratio on the basis of recent studies on coal distillates, but such vacuum distillate of coal may not represent the coal structure. It has been earlier shown<sup>34</sup> by the authors (and which has been recently confirmed<sup>56</sup>) that such distillates primarily originate from the alicyclic structure in coal (Fig.5).

### AROMATIC RING SIZE IN COAL

Coal is believed to have a polymeric or perhaps poly-condensate assemblage of structural units of varying dimensions. The measurement of the size of aromatic clusters in such structural 'units' is as important as the study of the state of combination of carbon and hydrogen. By oxidation studies the authors had also attempted an assessment of the average size of aromatic nuclei. According to the mechanism of oxidation suggested by the authors, the final oxidised residue of coal is believed to retain the aromatic skeleton of coal. Hence the atomic H/C ratio of the hypothetical unsubstituted aromatic skeleton corresponding to the oxidised coal would give a measure of the average size of the aromatic nuclei. It has been found<sup>27</sup> that the average size of aromatic nuclei does not vary much in the bituminous range (carbon: 80-90%) and is possibly constituted of 4 to 5 poly-condensed benzene rings per mean structural unit (Table 7). Earlier studies on x-ray diffraction<sup>3</sup> and on diamagnetic susceptibility<sup>24</sup> of coals led to similar assessments. Recent measurement of electron activation energy<sup>53</sup> also support the above estimates. In view of the consistency between the physical and chemical measurements (Table 7) it may, therefore, be concluded that possibly a fair estimate of the size of the aromatic units is now available.

Mild hydrogenolysis of coal extract, residue or coal itself by B.S. Biggs<sup>59</sup>, B.S. Biggs and J.F. Weiler<sup>60</sup> as well as by J. Le Claire<sup>61</sup> had also led to the recognition (1936-37) that the 'units' of coal structure must be small in size. The isolation of dodeca- and tetradeca-hydrophenanthrene and hexadeca- and octadeca-hydrochrysenes corresponding to 3-4 ring systems would now appear to be significant in the light of measurements of aromatic ring size by physical and chemical methods.

### DISCUSSION

The techniques of selective oxidation and pyrolysis in conjunction with dehydrogenation studies have possibly yielded the most acceptable information on the state of combination of carbon and hydrogen as well as on the size of the aromatic nucleus. The knowledge that has been acquired is summarised in Table 8.

Perhaps the time has now come for reorientation of the studies on the consti-

tution of coal. There are still many gaps in our knowledge which have to be bridged before the macro-molecular structural pattern of coal can be precisely depicted. Such problems that remain to be solved are :

- (i) Whether coal is a polymer in the typical sense;
- (ii) If so, what is the nature of the polymer, especially the nature of linkage between the 'units' of coal structure;
- (iii) The specific sizes of the individual structural 'units' of coal, in particular, the distribution of molecular weights among such 'units' which may not be all identical.

Information on the polymeric character of coal has been forthcoming from <sup>52</sup> studies on solvent extraction and those on hydrogenolysis. R.A.Glenn and co-workers, from a study of the liquid products obtained from hydrogenolysis, were led to conclude that coal structure has possibly repetitive units just as in a typical polymer. Confirmation of this polymeric concept has also possibly emerged from the recent studies of the authors<sup>63</sup> on the reaction of permanganate on coal. It has been shown that at any stage of degradation the residual coal left over after reacting coal with either acidic or alkaline permanganate retains virtually the same physical and chemical properties as that of the original coal (Table 9). This could perhaps be explained as a case of depolymerisation of the coal structure, followed by decomposition of the fragments into water soluble products like carbon dioxide, oxalic acid and benzene polycarboxylic acids.

The next stage is obviously to have adequate information about the actual repetitive 'units'. This can only be possible by isolation of the 'units' of coal by depolymerisation and determination of molecular weights of the 'units' thus isolated.

Another equally important knowledge to be sought is about the nature of linkage between the 'units'. Little or no information is available on this aspect at the moment. Studies on the mechanism of solvolysis of coal in organic solvents and of the dispersibility of coal in alkali (especially in lower ranks of coal) may reveal useful information.

In 1957 the authors<sup>64</sup> had indicated that the dissolution of lignite in alkali, even at room temperature is not merely a physical process but is probably preceded by hydrolytic splitting of bonds between the 'units'. It was suggested that in lignite (and in coal) the part that gives rise to humic acid and the residual part are possibly linked by flavone or similar type of linkage (e.g. pyrone, lactone, etc.) which are susceptible to cleavage in presence of alkali. However, it is premature to conclude anything definitely but it is believed that further work on these lines and others may throw greater light on this important aspect of coal structure. A fuller knowledge of the nature of the 'unaccounted' oxygen in coal vis-a-vis the dispersibility of coals in alkali, and of the mechanism of regeneration of humic acids from mature coals, may also be of help.

Besides the above basic considerations, we have yet to know more precisely about the character of nitrogen and sulphur. They are minor elements in coal but are believed to be integral parts of the coal structure. Information on the state of nitrogen has been scanty, though, of late, it has been suggested<sup>65</sup> that it may be largely present as functional groups. About sulphur, our knowledge is even less exact. The states of combination of these minor elements in coal are just as important as those of carbon and hydrogen.

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Table 1 - Verification<sup>42</sup> of the Oxidation Technique by the Determination of the Aromaticity of Reduced Coal Samples.

Sample No. & Particulars	%Analysis of the samples, d.m.f.		C	H	O	% loss or gain on oxidation	Analysis of oxidised samples, % d.m.f.			C	COOH	COOH	Carbon in oxidized samples, gm. Total Corrected for C <sub>COOH</sub> (C <sub>ar</sub> )	Aromaticity (C <sub>ar</sub> /C)	
	C	H					H	O	C					COOH	COOH
1. Original	85.7	5.2	6.4	--	--	--	--	--	--	19.0	7.1	55.9	49.7	0.76*	--
1A. Reduced	84.1	6.7	6.6	21	-12	63.5	2.1	32.2	19.0	7.1	7.1	55.9	49.7	0.59	0.55
2. Original	89.8	4.8	2.8	--	+7.4	73.1	2.1	22.3	13.0	4.9	4.9	78.5	73.2	0.82	--
2C. Reduced	86.1	7.3	4.1	35	-22.2	61.4	2.2	34.2	18.6	7.0	7.0	47.8	42.4	0.49	0.47

\* Oxidation done at 170°C for a prolonged period until there was no further oxidation. Generally this requires 1500 to 2000 hrs. in case of vitrains.

\*\* Theoretical aromaticity calculated on the basis of hydrogen that was added during reduction.

+ from pyrolysis; see Table 2.

\*\* Ethylene-diamine free analysis.

Table 2 - Validity of the Pyrolysis Technique in the Determination of the Aromaticity of Coal.

Sample No. & Particulars	Analysis		Pyrolysis (600°C)			Aromaticity, $\frac{C_{ar}}{C}$		$\frac{2(R-1)}{C}$ *
	C %	H %	H/C	V %	F %	Calculated from reduction data	Statistical* method	
1. Original	85.7	5.2	0.73	26.8	73.2	--	--	0.51
1A. Reduced	84.1	6.7	0.95	48.5	51.5	0.54	0.54	-do-
1B. "	83.4	5.8	0.84	40.7	59.3	0.63	0.65	-do-
2. Original	89.8	4.8	0.64	14.9	85.1	0.87	--	0.49
2A. Reduced	87.9	6.3	0.85	39.0	61.1	0.63	0.65	-do-
2C. Reduced	86.1	7.3	1.02	57.1	42.9	0.48	0.49	-do-

\* assuming that the ring-condensation index,  $\frac{2(R-1)}{C}$  of reduced coal would remain the same as in the original, the aromaticity of the reduced coals has been calculated from the formula:  $f_a = (1 - \frac{H}{C}) + 1 - \frac{2(R-1)}{C}$ . For the computation of ring-index of the original coals, however, the aromaticity determined by pyrolysis has been assumed to be correct.

Table 3 - Non-aromatic Carbon-Hydrogen Distribution in Typical Vitreous\*

(Reproduced in part from B.K.Mazumdar and A.Lahiri<sup>4,5</sup>)

Rank % C d.m.f.	Primary Data				Deductions **											
	+fha = Char C	e (i.r.) C <sub>CH</sub> +C <sub>CH<sub>2</sub></sub> %	a (n.m.r.) H <sub>CH<sub>2</sub></sub> %	Non-arom. hydrogen H <sub>CH</sub> %	Non-arom. carbon C <sub>CH<sub>2</sub></sub> %	Non-arom. carbon C <sub>CH<sub>3</sub></sub> %	b = Aromaticity fa	city	Aromaticity fa	city	Aromaticity fa	city	Aromaticity fa	city	Aromaticity fa	city
82.5	0.25	20.6	0.23	0.88	2.12	0.66	1.22	12.7	7.9	4.9	1.89	0.69	0.94	0.69	0.94	0.94
85.0	0.22	18.7	0.26	0.95	2.04	0.54	1.39	12.2	6.5	5.6	1.93	0.71	0.93	0.71	0.93	0.93
87.5	0.17	14.9	0.35	1.06	1.80	0.34	1.56	10.8	4.1	6.2	2.10	0.76	0.93	0.76	0.93	0.93
90.0	0.11	9.9	0.54	1.25	1.38	0.14	1.58	8.3	1.7	6.3	2.30	0.82	0.93	0.82	0.93	0.93

\* Deductions are shown in case of 4 out of 5 samples studied by Dryden<sup>66</sup>. The values of e, a and H<sub>0</sub> refer to his samples.

\*\* Subject to the assumption that all the tertiary CH and secondary CH<sub>2</sub> groups are embodied in the alicyclic structures.

+ Authors' maximum values of alicyclicity; see Fig.3 and also footnote in page 3.

Table 4 - Compatibility of the different estimates of aromaticity with those of Alicyclicity.

Rank % C, d.m.f.	Aromaticity, $f_a$		Preferred Values* of Alicyclicity (authors')		$f_a + f_{ha}$ Van Krevelen et al's ++	
	Statistical approaches (van Krevelen et al) 69	Chemical approaches (authors)†	$f_{ha}$			Authors
81.5	0.83	0.67	0.25	1.03	0.92	
85.0	0.85	0.70	0.22	1.07	0.92	
87.0	0.86	0.75	0.17	1.03	0.92	
89.0	0.88	0.80	0.12	1.00	0.92	
90.0	0.90	0.84	0.08	0.98	0.92	

\* from Fig.3. These values are considered to be the maximum; see footnote in page 3

† typical values from Fig.2.

++ the sum would still be higher if methyl-carbon is taken into consideration.

Table 5 - Comparative study of the three Methods of Dehydrogenation

Samples	Analysis		% of H removed during dehydrogenation	
	C	H	Sulphur (Vesterberg)	Iodine
<u>Vitrains</u>				
1	79.0	5.2	31	25
2	83.5	5.6	28	27
3	85.7	5.2	19	21
4	89.8	4.8	13	12
				26
				--
				20
				13
<u>Reduced Vitrains</u>				
1	86.1	7.3	43	44

\* Authors' assessment. 37

Table 6 - Selectivity of Sulphur (Vesterberg's) in the Dehydrogenation of the Hydroaromatic Structure in Coal 49.

Sample No. & Particulars	Analysis, d.m.f.	C	H	Field of		% of H removed		Extra H removed in case of reduced Samples	Alicyclicity, $\frac{C_{H_{10}}}{C}$	
				Reduced	Vibrain per 100 gm. starting vibrain	By S (Vesterberg)	by S (Vesterberg)		Found	Calculated
1	2	2	3	4	5	6	7	8	9	
2. Original Vibrain	89.8		4.3		-	12.6	-	0.08	-	
2c. Reduced**	86.1		7.3	104.4	2.67	43.4	2.68	0.45	0.45	
2d. Reduced**	86.1		5.9	104.3	1.30	52.1	1.23	0.26	0.25	

\* Compare column 5 with 7. This indicates the amenability of the hydroaromatic structure to complete dehydrogenation.

\*\* Ethylene-diamine free yield and analysis.

+ From the amount of H<sub>2</sub> formed without suspecting any side-reactions

\*\* The "theoretical" alicyclicity of reduced vibrains is based on the alicyclicity of the original vibrain and the extent of H-addition to it.

Table 7 - Average Aromatic Ring Size of Coal as Obtained by Different Approaches

Rank in C, d.m.f.	Aromatic ring size by oxidation technique 27,40										No. of benzene rings per mean structural unit from	
	H	O	OH	CO	COOH	C-O-C	H/C exp. atomic	atomic H/C of unsubsti- tuted aromatic nucleus of coal	No. of benzene rings per ave- raged struc- tural unit.	A-ray Diag- netic Suscep- tibility	Statistical Methods (van Krävelen et al 69)	
81.5	65.4	2.3	30.0	4.0	6.5	16.0	5.5	0.41	0.63	4	4.4	
84.4	65.5	2.5	29.0	2.6	7.9	15.9	2.6	0.41	0.62	4	4.7	
87.3	67.6	2.2	28.2	2.2	9.0	14.0	3.0	0.39	0.60	4.5	2-5*	
89.3	72.9	2.6	22.1	1.0	11.3	8.0	1.8	0.41	0.60	4.5	5.0	
89.6	70	2.2	25.2	1.5	11.0	11.2	1.5	0.38	0.57	5	5.2	
93.2	88.1	2.6	7.4	2.1	2.4	2.1	0.8	0.35	0.39	12-15	12	
												6.5

\* This represents the range of assessment rather than the average size. Measurements have also indicated that the average number of atoms per layer varies from about 14 atoms at 78% C to about 18 atoms at 90% C and about 36 atoms at 94% C. These would excellently correspond to the number of benzene rings per layer estimated from oxidation studies.

Table 8 - A Summary of the Essential Structural Parameters of Coal\*

Typical Vitraains		Distribution of carbon		Distribution of hydrogen		Distribution of benzene rings				
C	H	H/C	fa**	fhar**	fal (C-CH <sub>3</sub> ) By diff.	*** H <sub>2</sub> %	**Har H <sub>2</sub> O	H <sub>2</sub> Har*** H <sub>2</sub> O	††No. of benzene rings per mean structural unit.	
81.0	5.4	0.80	0.67	0.25	0.08	5.0	0.23	0.45	0.32	4
82.5	5.3	0.77	0.68	0.24	0.03	4.9	0.25	0.42	0.35	4
85.0	5.4	0.76	0.71	0.22	0.07	5.1	0.29	0.41	0.30	4
87.5	5.3	0.73	0.75	0.17	0.08	5.2	0.33	0.35	0.32	4.5
90.0	4.8	0.64	0.82	0.11	0.07	4.7	0.46	0.20	0.34	5
93.2	3.5	0.45	nil	nil	0.03	3.5	0.80	nil	0.20	12

\* The distribution of C and H in different forms had also been earlier<sup>33,39,40</sup> presented but the present one is considered to be more accurate.

\*\* maximum aromaticity and alicyclic values from oxidation and dehydrogenation studies respectively.

+ mean of physical and chemical determinations.

†† calculated from methyl carbon

††† obtained by difference; this would be found to be largely consistent with the detailed distribution of hydrogen in CH and CH<sub>2</sub> forms recently deduced<sup>45</sup> by the authors from i.r. and n.m.r. data (Table 3).

\*\*\* % H less 'hydroxyl' hydrogen.

Table 9 - Comparative Analysis of Coals and Permanganate Treated Coals at different Stages of Degradation.

Reproduced from A. Banerjee, B. K. Mazumdar and A. Lahiri <sup>63</sup>7

Sl. No.	Analysis of Coal, d.m.f.			Nature of coke button (original coal)	Time of treatment with $KMnO_4$ in hrs. (at room temperature)	%Loss of organic matter	Analysis of Treated Coal d.m.f.			Nature of coke button (treated coal)
	C	H	%				C	H	%	
1.	69.2	4.5	--	medium hard	** 0.5	67.2	69.6	4.8	--	--
2a.	81.8	5.4	29.6	greyish bead	0.5	19.4	81.0	5.3	--	--
b.	"	"	"	"	1.0	25.9	81.6	5.5	30.4	weak but coherent
c.	"	"	"	"	2.0	36.3	82.1	5.4	30.1	-do-
d.	"	"	"	"	24.0	36.1	81.2	5.5	31.5	-do-
e.	"	"	"	"	** 0.5	27.0	81.3	5.4	--	--
f.	"	"	"	"	** 0.5**	83.1	80.0	5.5	--	--
3.	86.7	5.3	-	Highly swollen porous coke.	1.0	23.7	86.5	5.3	--	Medium hard porous coals
4a.	89.9	4.9	14.9	"	1.5	14.5	89.1	4.7	14.1	Highly swollen porous coke.
b.	"	"	"	"	2.5	14.3	89.3	4.7	14.8	-do-

+ All vitrain samples. \*\* In contrast to the preceding experiment, in this case, more than 60% of the coal could be converted into soluble products because of 3 successive treatments of 10 minutes duration each, instead of a single treatment.

\* different concentration of  $KMnO_4$ , alkali or acid and varying ratio of  $KMnO_4$  to coal were used. This is of no consequence in respect of the analysis of the treated coals.

\*\* dil.  $H_2SO_4$  acid medium and the rest, alkaline.

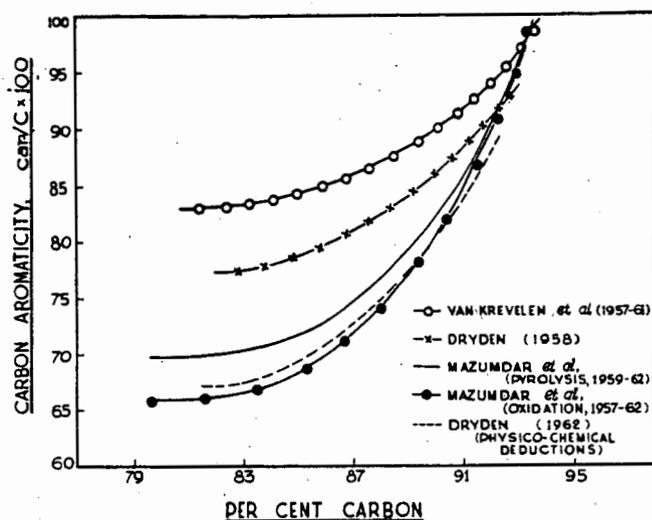


Fig. 1 - Aromaticity of coal by different approaches.

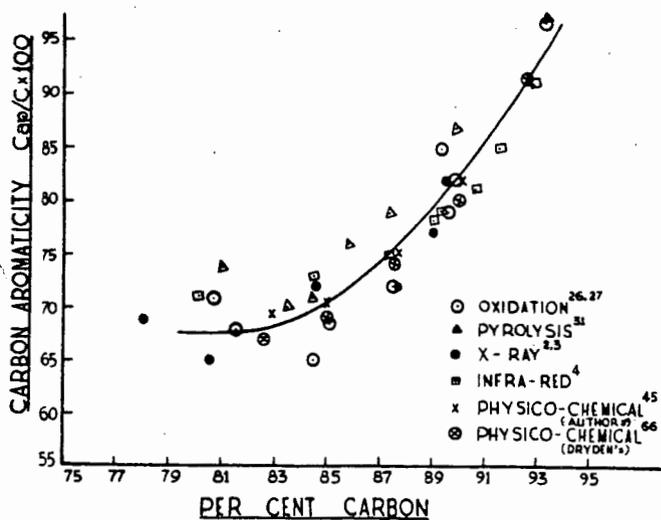


Fig. 2 - Mean aromaticity of coal and its variation with rank as determined by chemical methods and its comparison with values from some of the physical and physico-chemical approaches.

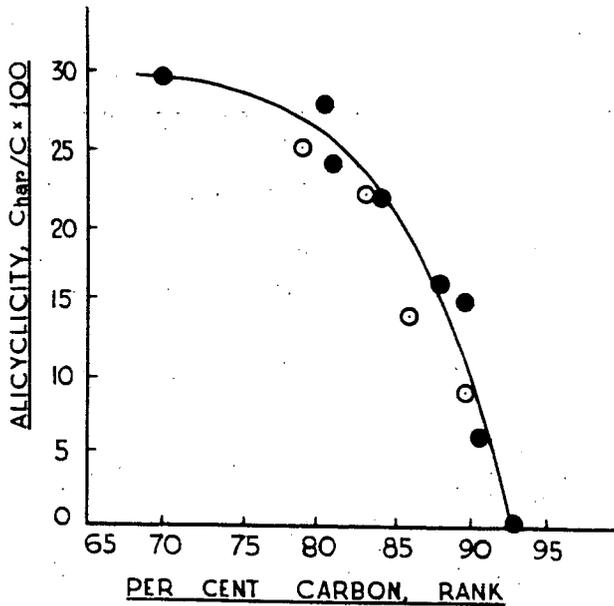


Fig. 3 - Variation of the alicyclicity of coals with rank  
 ● - values obtained in 1952 by dehydrogenation with sulphur<sup>32,33</sup>; ○ some recent determinations.

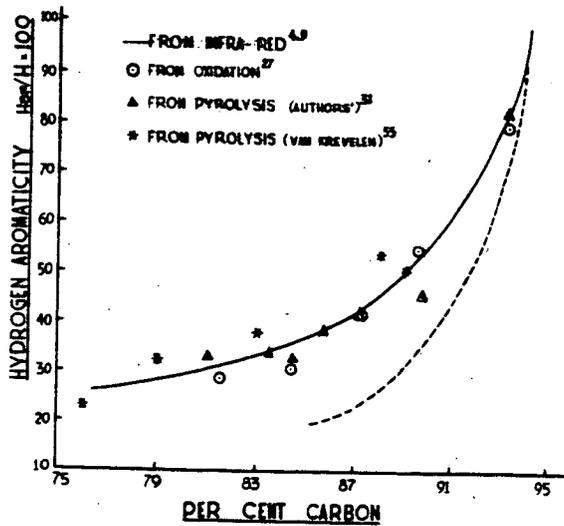


Fig. 4 - Variation of the hydrogen aromaticity with rank : a comparison of the physical and chemical estimates.

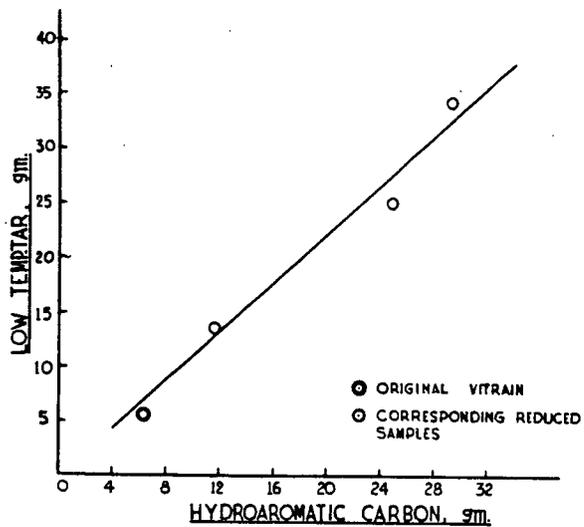


Fig.5 - Role of hydroaromatic structure in the formation of tar.  
[reproduced from Ganguly, S., Mazumdar, B.K. and Lahiri, A.<sup>56</sup>]