SOME ASPECTS OF THE CONSTITUTION OF COAL

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The last ten years have witnessed rapid strides in our knowledge of the complex nature and constitution of coal. The recent contributions from the physical techniques e.g. infra-red, nuclear magnetic resonance, X-ray and van Krevelen et al's statistical approaches have given a new impetus to the study of coal science as a result of which various models[1,2] of the structural 'unit' of coal have been suggested from time to time. However, the problem of coal constitution is ultimately a chemical one and in the long run sanction of chemical approaches have to be sought for any structure proposed for coal, irrespective of the technique employed in formulating the model. In the past, extensive studies on the oxidation, reduction, halogenation, pyrolysis etc. of coal had been carried out but the data, through informative, failed to unravel the intricate chemical structure of coal in the orthodox chemical sense, nor did they yield any significant information on the structural parameters of coal, an essential prerequisite for hypothesizing a model structure. However, as a result of recent studies an attempt may now possibly be made to make tentative proposals based on the information on the state of carbon, hydrogen and oxygen in coal[3-13].

Oxygen in Coal

Though there is still divergence of opinion regarding the actual values of hydroxyl, carbonyl and carboxyl oxygen groups in coal, a fair order of estimate particularly for hydroxyl is now available[14]. 50-60 per cent of the total oxygen in coal, at least in lower ranks ($C < 85-86\%$) is found to be in the form of hydroxyl groups, and the rest appears to be present in small amounts as carbonyl, carboxyl and ether and/or heterocyclic oxygen groups. In higher rank coals ($C > 86\%$) few of the functional oxygen groups are believed to be present, but the major part of oxygen remains unaccounted for.

State of Carbon and Hydrogen in Coal:

Oxidation & Dehydrogenation Studies: The work of Bone, Wheeler and their collaborators[15] in the early twenties and of Horton[16] and others established that aromaticity of coals increased with increase of the rank. But, for precise determination of aromaticity obviously a method of controlled oxidation was needed which would selectively oxidise the non-aromatic part of the coal structure. Such a method of oxidation was recently advanced[4] by the present writers. It was shown that prolonged oxidation of coal in air at 170°C was chiefly restricted to the non-aromatic structures of coal, leaving the aromatic carbon skeleton practically intact. Such an approach, supported by further work[5,17] led to a number of deductions regarding aromaticity, forms of hydrogen, the size of the aromatic nucleus, and an assessment of the dimensions of the aliphatic side-chains in a coal unit. These deductions are presented in Tables 1 and 2.

The recent studies on dehydrogenation[10,11,12,13] of coals have thrown some fresh light on the problem. The non-aromatic carbon structure of coal has so far been assumed to be only aliphatic in nature. Dehydrogenation studies by Vesterberg's technique and with halogens[18], appear to indicate that the non-aromatic part may be largely constituted of alicyclic carbon. Similar indications have since been obtained by Ergun[19] from x-ray studies.

The presence of hydroaromatic or alicyclic structure was, however, first suggested by Weiler[20] on the score of the dehydrohalogenation phenomenon (which he called "spitting").

Quantitative measurement of alicyclic carbon and hydrogen from dehydrogenation studies show that a considerable proportion of carbon in bituminous coal is in alicyclic form (10-25%) and also that the alicyclicity progressively diminishes with increase in the rank of coal. Anthracite does not contain any alicyclic carbon nor does it undergo any dehydrogenation.

The chief objection[21] to this technique (Vesterberg's) for quantitative measurement of alicyclicity of coals has been that the method may not selectively dehydrogenate alicyclic carbon alone and that aromatic carbon may also be affected to some degree. Further studies[13] have, however, shown that only a minor part of dehydrogenation may be due to some side-reactions (possibly cross-linking) with aromatic positions and there does not appear to be any doubt, that the method is fairly reliable (as far as coal is concerned). Corrections have now been made for such possible stray side-reactions and the new set of values for alicyclicity of coal derived, are presented in Table 3.

It may appear strange, but statistical and experimental facts seem to indicate that the sum of aromatic and alicyclic carbon percentage is virtually constant (0.87 ±0.03) as will be seen from Table 4.

If this be true, then obviously the value for the percentage of aliphatic carbon can be deduced from experimentally determined values of aromaticity and alicyclicity, and naturally the value for aliphatic carbon percentage in coals will also be nearly constant. This value is between 10-15% : it may, however, be somewhat on the higher side, as it is likely that the values for alicyclicity presented here is likely to err on the minimum side. Be that as it may, the constant nature of the aliphatic carbon in coal (if this be the case) would appear to be a remarkable fact, for which no explanation can be offered at this stage.

It was suggested[9] earlier that the aliphatic side-chains present in coal should be small and even as small as in methyl group, and certainly not longer than in an ethyl group. The estimation of C-methyl content by Kunn and Roth's reaction[22,23,24] yielded a value of 2 to 4% of the carbon present as methyl group in coal. It is possible that this value is also on the lower side, as the aromatically linked methyl group may not be estimated quantitatively by this technique[25]. Exhaustive chlorination[26] on the other hand gave a higher estimate of C-methyl content i.e., 6-7% of the carbon. The agreement between the experimental values and those theoretically deduced as far as the order is concerned may or may not be significant. Further refinement in the techniques of determination of aliphaticity in coals should prove to be of great value.

The Alicyclic Structure in Coals

The formation of tar is completely inhibited when a dehydrogenated coal is carbonized. There is, also, a proportionate increase in the yield of char. The additional carbon 'fixed' in the char is apparently proportional and almost equal in value to the alicyclic carbon estimated directly[10,11,13]. Therefore, it may not be illogical to conclude that tar has its origin in the alicyclic structures of coal[12]: The complete inhibition of tar formation by any method of dehydrogenation (even by air/oxygen)[27] is also significant.

van Krevelen and Fitzgerald recently concluded[28] that "that part of coal structure which yields tar must be weakly linked or not at all bonded to the remainder". A study on the extent of the inhibition of tar formation with varying degrees of dehydrogenation (Fig.1) also leads to a similar conclusion[13]. The complete inhibition of tar formation, however, does not appear to depend on the completeness of the dehydrogenation but a minimum quantity of the dehydrogenating agent (sulphur) is apparently needed for the maximum inhibition (Fig.1). It appears probable that simultaneously with dehydrogenation, a condensation reaction (possibly by cyclo-dehydrogenation) between the alicyclic part and the rest of the coal structure is possibly initiated. The action of sulphuric and

phosphoric acids[29], phosphoryl oxychloride[30], even Scholl's reagent[31] also appear to have similar effects on inhibition of tar formation and probably through a similar mechanism of condensation reaction, leading to fixation of the alicyclic carbon in the char.

Another significant fact is that on dehydrogenation or even in condensation reactions mentioned above, nearly 92% of the total carbon in coal is found to be retained in the char (600°C) on carbonization, irrespective of the rank of coal so treated from lignite upto the high rank bituminous coals. Normally, in carbonization only 70-80% of the carbon is fixed in the coke or char at 600°C. Thus, the 'extra' carbon retained in char is of the order of 10-22% of the total carbon in coal, which corresponds to the values of alicyclicity of coals determined directly by dehydrogenation reactions. The proportion of carbon normally fixed in coke and char on carbonization at 600°C corresponds to the aromatic carbon in coal[32]. The additional carbon fixed on treatments mentioned above and the constancy of the value at about 92 %, again, appears to correspond to the sum of aromatic and alicyclic carbon, irrespective of the rank of coal.

This would indicate that in course of coalification enrichment of aromatic carbon takes place at the expense of alicyclic carbon (and possibly derived from it), the sum total of the two being constant.

Stages in Coalification :

The progressive increase in aromaticity in coal (at the expense of alicyclic carbon) during coalification must be a very slow process and a gradual one. One may, therefore, envisage a 'parent' coal unit at any particular stage of evolution which will vary in aromaticity, alicyclicity and ring size. This concept of the evolution of coal with increasing rank may be hypothetically illustrated in terms of the structural models shown in Fig. 2.

The model I, C = 68 %, may be arbitarily assumed to be the 'parent' structural unit of coal, existing in the lignitic stage (there may be other structural units, but the model I may be conceived to be as the predominant species at this level). Decarboxylation and partial dehydroxylation (which are believed to be the major reactions in the evolution of coal in the lower ranks) of model I can lead to the stage of model II, C = 79 %. The model IIIA, C = 91 % is envisaged to be the transitional stage marked by the completion of the decarboxylation, dehydroxylation and dehydrogenation of the alicyclic ring and its fusion with the aromatic nucleus. Partial demethylation may also occur between the stage II and IIIA.

The transitory nature of these structures is to be emphasised at any particular stage of the rank evolution of coal. Decarboxylation may be largely completed at or near about 80% carbon coal but the process may continue well after this stage is reached. Small amounts of carboxylic oxygen can still be detected even in 84-85 % carbon coal. Dehydrogenation of the alicyclic ring and ring-closure by cyclodehydrogenation (model II & IIIA) may constitute the major steps in the bituminous coal range.

The properties of the three hypothetical structures designed to portray the three important transition steps in rank-evolution may be depicted as in Table 5.

The analysis of structure IIIA (Table 5) broadly represents a typical high rank bituminous coal (C = 91 %) having 91% aromatic carbon. This 'unit' given in the model is presumed to be the most predominant one present at 91% carbon level. At any intermediate stage of coalification between lignite and this high rank bituminous coal, a certain fraction of the 'unit' of model I may undergo metamorphosis into the 'unit' of model II which in its turn, under the prevailing geo-chemical condition may undergo further progressive transformation into the model IIIA. The final stage (model IIIA) is, thus, a result of the sum total of decarboxylation, dehydroxylation, dehydrogenation and partial demethylation of the 'parent' unit (model I). The incipient initiation of stage II to IIIA reaction in

the earlier stages is also not precluded. As a result, any transitory stage in rank-evolution may contain a mixture of one or two or all of the above types of units, though one or the other model species may predominate, depending upon the level of geochemical metamorphosism attained in the natural state.

No coal can, therefore, be homogeneous in respect of their unit structures. As an example, a proportion of 10:70:20 of the three structures may represent the typical analysis, both chemical and structural, of a 80% carbon coal (Table 5). Such a plausible structural analysis of a 80% carbon coal would indicate that it has undergone substantial decarboxylation. It would also indicate that dehydroxylation, dehydrogenation, (including cyclo-dehydrogenation) and demethylation processes had been initiated in varying degrees. All the transformations are consistent with the known properties of coal of such a rank. A partial conversion of model II to IIIA (say to the extent of 22% as suggested in the proportion of the units) will lead to an increase in aromaticity and also to the growth of the aromatic nucleus at the expense of alicyclic carbon.

The possibility of a number of model species (units) occurring together at any stage of coalification (though one or the other may be the dominant one) may also explain some of the following observations: (1) the assortment of ring sizes in any coal, (2) the constant trend of the sum of aromaticity and alicyclicity in any rank of coal (lignites and bituminous coal), (3) the constancy of carbon per cent retained in the char of dehydrogenated coal samples of any rank, as well as several other apparently perplexing facts observed in course of our studies on dehydrogenation and cyclo-condensations.

Whereas the transition of stage I to stage IIIA depicts the evolution of normal coals upto the highest rank in the bituminous range occurring under a set of geochemical conditions, the transition of stage III to stage IV (anthracite stage) must, by all accounts, be an abrupt and drastic one, involving a completely new set of geochemical conditions. The evolution of a typical anthracite may be conceived as shown in Fig. 3.

The structural models given here are not intended to actually represent any coal but has merely been used to illustrate the concept of the heterogeneity of the coal structure at any particular stage, and to emphasise the predominant chemical transmutation that may take place in response to geochemical forces in nature at any given level of metamorphic history of coal.

Studies in rank classification of coal have led to the formulation of the well-known coal band, which by itself, emphasises the transitory nature of the metamorphic changes in coal. Whether there are distinct and discretely separate zones of chemical reactions in course of rank-evolution is yet to be established, though the predominance of one set of reactions over another at any stage can not be disputed.

Admittedly, the models, the reactions, and the concept of co-existence of several models may explain many experimentally determined properties of coal, but we do not submit them here as pure "models" of any 'unit' coal; that stage may yet be far off. The number of rings assumed or other structural feature shown in the models (e.g. the disposition of unaccounted oxygen) may be different and still fit into the general picture of evolution of rank, but what is emphasised is that rarely any reaction in nature is ever complete, though the ideal is always towards perfection.

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Table 1 - Calculation of Aromaticity in Coal from Oxidation Studies
(Based on oxidation of 100 gm. of coal substance)

[Reproduced from Chakrabartty, S.K., Mazumdar, B.K., Roy, S.N., Lahiri, A., Brennst-Chemie, in press]

Sample	C %	H %	Gain/ loss in wt. %	Oxygenated groups in oxy-coal				Carbon input gm.	Carbon output gm.	C_{COOH} (in oxy-coal) gm.	% aromatic (C_{ar})	$\frac{C_{ar}}{C_{total}}$
				O_{COOH} %	O_{OH} %	O_{CO} %	O_{COC} %					
Lignite	71.53	4.66	-26.4	17.5	7.4	4.0	6.2	71.53	45.23	4.83	40.40	0.56
Overall(1)	80.69	5.33	-8.0	14.3	2.3	6.5	5.0	80.69	62.38	4.93	57.45	0.71
Vitrain (1)	81.46	5.40	-7.0	16.0	4.0	6.5	3.5	81.46	60.82	5.58	55.24	0.68
Vitrain(2)	84.35	5.72	-7.6	16.0	2.6	7.9	2.6	84.35	60.56	5.52	55.04	0.65
Overall (2)	85.15	5.70	-5.0	14.3	4.0	5.3	4.4	85.15	63.86	5.10	58.76	0.69
Vitrain (3)	87.25	5.27	+0.8	14.0	2.2	8.9	3.0	87.25	68.08	5.28	62.80	0.72
Vitrain (5)	89.56	4.98	+8.0	11.2	1.5	11.0	1.5	89.56	75.60	4.56	71.04	0.79
Overall (3)	90.31	4.86	-2.9	10.3	3.0	4.4	2.0	90.31	73.79	3.75	70.04	0.78
Anthracite	93.20	3.50	+4.0	2.1	2.1	2.4	0.8	93.20	91.60	0.83	90.77	0.97

Table 2 - Forms of Hydrogen and Average Ring-size of Coal Units from Oxidation Studies
(Based on oxidation of 100 gm. coal-substance, d.a.f.)
[Reproduced from Chakrabartty, S.K., Mazumdar, B.K., Roy, S.N., & Lahiri, A., Brennst-Chemie, in press]

Sample	Rank C %	Atomic H/C.	Hydrogen input gm.	Hydrogen output gm.	Correction for H_{alip}* gm.	Correction for H_{arom}** gm.	H_{ar}+ gm.	$\frac{H_{ar}}{H}$	$\frac{H_{nar}}{H}$	atomic H/C oxycoal	Atomic H/C (hypothetical hydrocarbon corresponding to the oxy-coal)	*** No. of rings Cata-condensed	*** No. of rings Peri-condsd.
Lignite	71.53	0.78	4.66	1.77	-0.40	Nil	1.36	0.29	0.71	0.47	0.75	-	-
Overall (1)	80.69	0.79	5.33	1.93	-0.41	+0.27	1.79	0.32	0.67	0.37	0.60	7	5
Vitrain (1)	81.46	0.79	5.40	2.10	-0.47	+0.26	1.89	0.35	0.65	0.41	0.63	5	4
Vitrain (2)	84.35	0.81	5.72	2.09	-0.46	+0.43	2.06	0.36	0.64	0.41	0.62	6	4
Overall (2)	85.15	0.80	5.70	2.25	-0.43	+0.30	2.12	0.37	0.63	0.42	0.63	5	4
Vitrain (3)	87.25	0.72	5.27	2.20	-0.44	+0.50	2.26	0.43	0.57	0.39	0.60	7	5
Vitrain (5)	89.56	0.63	4.98	2.41	-0.38	+0.74	2.77	0.55	0.44	0.41	0.60	7	5
Overall (3)	90.31	0.65	4.86	2.33	-0.31	+0.25	2.27	0.47	0.53	0.38	0.49	-	7
Anthracite	93.20	0.47	3.50	2.70	-0.07	+0.016	2.79	0.80	0.20	0.35	0.39	-	12

* H Corresponding to COOH, See Table 1.
** H replaced by quinone gr., see Table 1
\+ This includes the hydrogen of the phenolic hydroxyl group.
*** Calculated from the hypothetical atomic H/C ratio corresponding to the 'hydrocarbon' model of the oxidised coal.

Table 3 - Values of Alicyclicity determined by Dehydrogenation Studies

(Based on dehydrogenation of 100 gm. coal substance by sulphur)[10,11,13]

[Data mostly reproduced from 'Further Studies on Dehydrogenation of Coal'[13], Fuel, in press]

Sample	C %	H %	H % dehydrogenated from alicyclic positions *	Total alicyclic H (H_{ha}) gm.	$\frac{H_{ha}}{H}$	Total alicyclic (C_{ha}) gm.	$\frac{C_{ha}}{C}$ = alicyclicity	** % of carbon retained in 600°C: Normal coal	** % of carbon retained in 600°C: Dehydrogenated coal	$\frac{C_{ha}}{C}$
Lignite	71.53	4.66	-	-	-	-	-	68	91.0	0.23
Overall (a)	80.10	5.44	23.5	2.55	0.47	15.30	0.19	75	92.0	0.17
Overall (1)	80.69	5.33	22	2.35	0.44	13.50	0.17	75	95.0	0.20
Vitrain (1)	81.46	5.40	20	2.16	0.40	12.96	0.16	74	92.0	0.18
Vitrain (2)	84.35	5.72	16	1.83	0.32	10.98	0.13	70	87.0	0.17
Overall (2)	85.15	5.70	16.5	1.88	0.33	11.28	0.13	71	87.0	0.16
Vitrain (3)	87.25	5.27	12	1.27	0.24	7.62	0.09	78	92.0	0.14
Vitrain (5)	89.56	4.98	10	1.00	0.21	6.00	0.07	86	92.0	0.06
Overall (3)	90.31	4.86	14.5	1.43	0.29	8.58	0.10	82	95.0	0.13
Anthracite	93.20	3.50	nil	nil	nil	nil	nil	98	98.0	nil

* After correcting for "side-reactions" with aromatic positions shown elsewhere[13]. The corrections may be on the higher side and the values of alicyclicity presented here should be treated as the minimum estimate.

** Taken from earlier papers[10,11]

Table 4 - Structural Parameters from Oxidation[9], Dehydrogenation[13] and Pyrolysis[32]
(Typical values of aromaticity, alicyclicity and aliphaticity)

Sample	C %	H %	Distribution of Carbon			Distribution of Hydrogen		
			** Aromaticity $\frac{C_{ar}}{C}$	Alicyclicity $\frac{C_{ha}}{C}$	Aliphaticity $\frac{C_{al}}{C}$ (by diff.)	$\frac{H_{ar}}{H}$	$\frac{H_{ha}}{H}$	$\frac{H_{al}}{H}$ (by diff.)
Lignite	71.53	4.66	0.62	0.22	0.16	0.30	0.50	0.20
Overall (1)	80.69	5.33	0.72	0.18	0.10	0.35	0.45	0.20
Vitrain (1)	81.46	5.40	0.71	0.17	0.12	0.35	0.43	0.22
Vitrain (2)	84.35	5.72	0.68	0.15	0.17	0.34	0.36	0.30
Overall (2)	85.15	5.70	0.70	0.15	0.15	0.35	0.36	0.29
Vitrain (3)	87.25	5.27	0.75	0.11	0.14	0.43	0.30	0.27
Vitrain (5)	89.56	4.98	0.82	0.07	0.11	0.50	0.20	0.30
Overall (3)	90.31	4.86	0.83	0.05	0.12	0.49	0.13	0.38
Anthracite	93.20	3.50	0.97	nil	0.03	0.82	nil	0.18

** Average values on the basis of oxidation[9] and pyrolysis[32] studies.

Table 5 - Comparison of the Chemical and Structural properties of the suggested Structural Pattern with those of a typical Coal

Analysis	Model I	Model II	Model IIIA	Assembly of structure with 10% of Model I, 70% of Model II, 20% of Model IIIA	Coal C = 80% (Typical value)
+ Empirical formula	$C_{24}H_{24}O_{6.7}N_{0.5}$	$C_{23}H_{22}O_{2.7}N_{0.5}$	$C_{22}H_{12}O_{0.5}N_{0.5}$	-	-
Unit wt.	426.2	348.2	291	-	-
C%	67.6	79.3	90.7	80.4	80.2
H%	5.6	6.4	4.1	5.7	5.4
N%	1.6	2.0	2.4	2.0	1.9
O%	25.2	12.3	2.8	11.9	12.5
O_{COOH}%	7.5	Nil	Nil	0.8	0.9
O_{OH}%	11.3 } 15.1	4.6 } 9.2	Nil	4.4 } 8.0	6.0 } 7.8
O_{CO}%	3.8	4.6	Nil	3.6	1.8
*O_{C-O-C}%	2.6	3.1	2.8	3.1	3.8
f_a (aromaticity)	0.58	0.61	0.91	0.67	0.68
** f_{ha} (alicyclicity)	0.29	0.30	Nil	0.24	0.18
f_{al} (aliphaticity)	0.13	0.09	0.09	0.09	0.14
*** $\frac{H_{ar}}{H}$	0.21	0.17	0.60	0.26	0.35
$\frac{H_{ha}}{H}$	0.50	0.55	-	0.44	0.45
$\frac{H_{al}}{H}$	0.29	0.28	0.40	0.30	0.20
Average No. of aromatic Rings	3	3	5	3.5	4

* In the models, the unaccounted oxygen usually found in coals have been represented as ether linkages: this may not be true. On the other hand, the possibility of the heterocyclic oxygen in coal in the form of flavone[33] structure or similar configuration can not be ruled out (unpublished work : Mazumdar, B.K. et al). No attempt is made now to represent this in the models.

** This includes the bridge methylene group.

*** This includes the hydrogen of the phenolic hydroxyl group.

\+ Proportion of nitrogen assumed; its disposition in the models has not been shown.

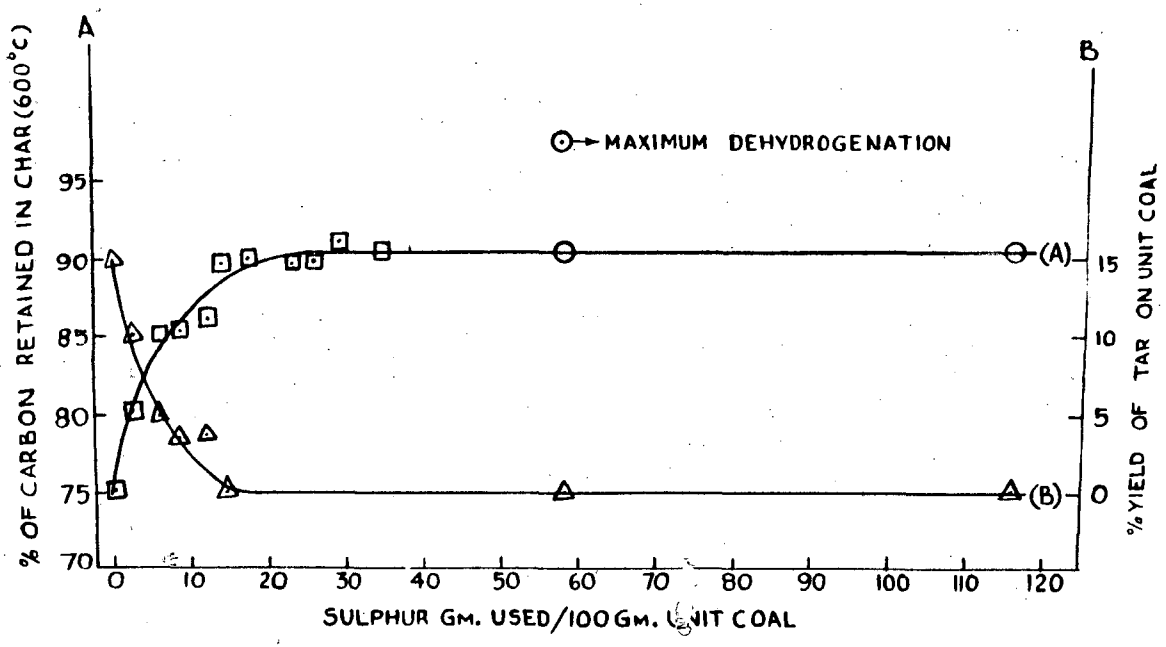
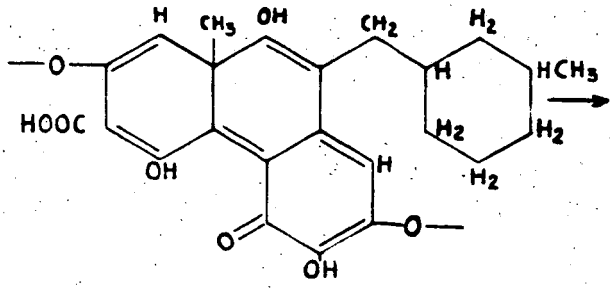
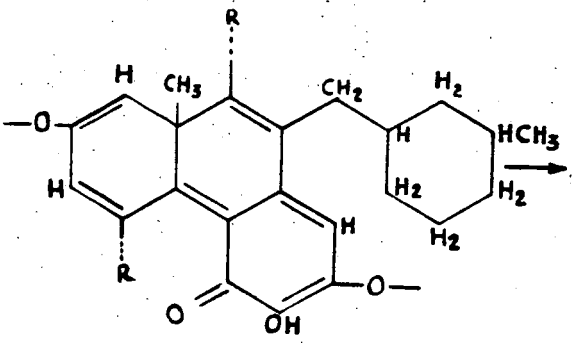


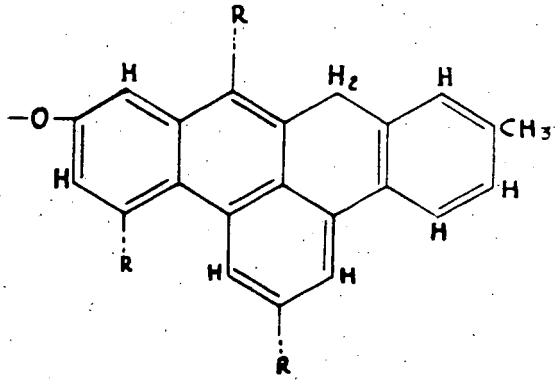
Fig. 1 Inhibition of Tar Formation and Fixation of Additional Carbon in Char consequent on Varying Degrees of Dehydrogenation.



I
C=67·6%

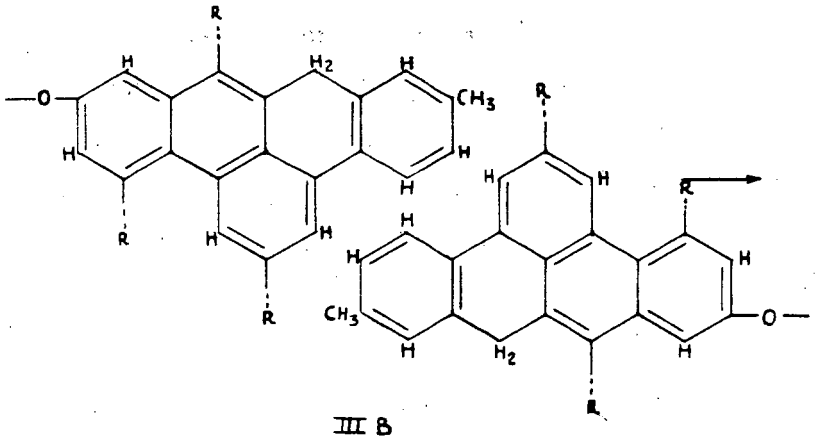


II
C=79·3%

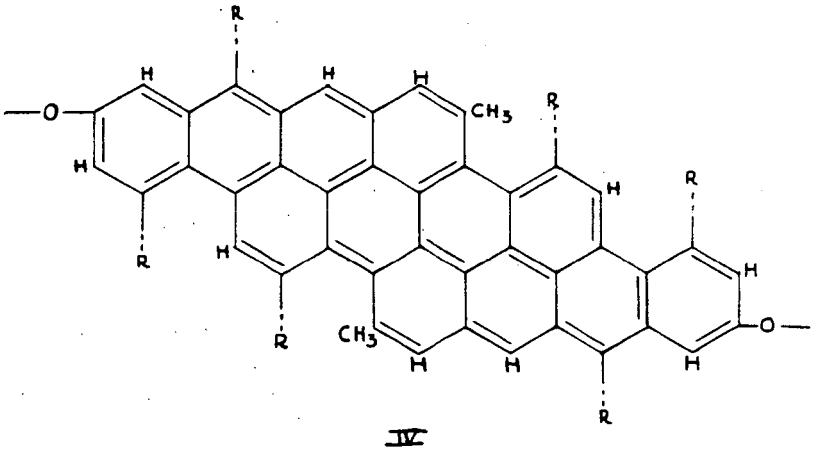


III A
C=91·0%

Fig. 2 Hypothetical model Unit illustrating its Transition from the stage of Lignites to High Rank Bituminous Coal.



III B
C = 91·0%



IV
C = 94·0%

Fig. 3 Hypothetical Model Units depicting the Formation of Anthracite from the Stage of High Rank Bituminous Coal.

Model IV : Empirical formula : $C_{44}H_{18}O_{0.7}N_{0.5}$
Unit wt. = 562.2, C = 94.0, H = 2.8
N = 1.2, O = 2.0, f_a = 0.95.

Typical analysis of anthracite, C = 94.3, H = 3.0, N = 1.0, O = 1.7