

FRACTIONATION OF SOLUBLE PORTION OF REDUCTIVELY ALKYLATED BITUMINOUS COALS

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Received February 4th, 1985

Five bituminous coals were reductively alkylated with potassium and 1-butyl iodide in THF. The benzene soluble portion of reductively butylated coal were separated into the saturates, aromatics, neutral heterocyclics, ethers and polar compounds on a silica gel column. From the saturates, the n-alkanes were isolated by the thin-layer and column chromatography on silica gel, and then analyzed by GC. The aromatics were fractionated on a dual packed SiO₂/Al₂O₃ column. The mono- and diaromatic fractions obtained were studied by GC-MS method. The non-hydrocarbon and polar compounds were characterized by elemental composition, VPO molecular weight and both IR and ¹H NMR spectra. The asphaltenes from one reductively butylated coal were fractionated into basic and acidic/neutral parts after bubbling dry HCl gas through their benzene solution. A concept that benzene eluates collect C-alkylation products and diethyl ether + THF mixtures collect the products of O-alkylation was evolved. The ratio of C-alkylation to O-alkylation was found to be a function of the C content of the initial coals.

An efficient method for coal vitrain conversion into a soluble state was suggested more than ten years ago by Sternberg and coworkers.¹ An improved procedure for reductive alkylation was reported by Lazarov and coworkers² based on directly prepared ionic potassium-coal adducts thus overcoming some of the problems of Sternberg's method. This technique made it possible to reveal some differences in the behaviour of different rank coals which were unnoticeable when the potassium-naphthalene-tetrahydrofuran system was used. In previous studies^{3,4}, it was found that bituminous coals with carbon contents in the 85–90% range formed considerable concentrations of alkylatable radical anions, the heterogeneous polymer analogues of polycyclic aromatic hydrocarbons having a lamellar structure and porosity. The lack of by-products of the electron-transfer agent is an advantage of this technique and will facilitate investigations with structural goals.

A search for a suitable method for fractionation of the soluble product of alkylation is desirable. A procedure eliminating tetrahydrofuran (THF) cleavage products and naphthalene derivatives by direct extraction with ethanol was employed¹. Larsen and Urban⁵ have utilized a column chromatographic procedure: n-Hexane, n-hexane-benzene (1 : 1) and THF served as eluents to separate the material into

6 fractions. The first three fractions were the products of reduction and alkylation of naphthalene and were inconvenient for investigations. The fifth fraction was obtained by vigorous treatment of the column adsorbent with NaOH concentrated solution and after this the organic mass was benzene extracted. The irreversible bound part of a sample to the adsorbent reached almost 8 wt. %. As a result about one-half of the products could be related to the initial coal structure.

To obtain the molecular mass distribution, gel permeation chromatography (GPC) was widely applied on a large scale separation of total extracts on μ Styragel columns^{1,6}, on soft gels Sephadex LH-20 or LH-60⁷⁻¹⁰, and on Bio Beads S-X type¹¹⁻¹³.

In their first study, Sternberg and coworkers¹ drew attention to a similarity in the tendency for formation of "anions" and the molecular mass of low volatile bituminous (lvb) coals and petroleum asphaltenes. They concluded that conversion of lvb coal into benzene-soluble state by adding an alkyl group indicated that the difference between the coal and petroleum asphaltene should be sought not in the molecular size but in the molecular structure. Bearing in mind similar concept, Miyake and coworkers¹⁴ and Kikkawa and coworkers¹⁵ fractionated the soluble portion of reductively alkylated coals in a manner adopted from studies on liquids obtained from hydrogenation of the same coals. By exhaustive Soxhlet extraction the material was divided into pentane-soluble and insoluble parts.

The present work is devoted to a study of available methods for preparative fractionation of the soluble portion of reductively alkylated bituminous coals in fractions convenient for further investigation by instrumental methods.

EXPERIMENTAL

The coal samples were bituminous coals from the various mines: 1. Westerholt mine, seam F (F.R.G.); 2. ČSM Ostrava mine, seam 14 (Czechoslovakia); 3. Balkanbass mine, Divina seam (Bulgaria); 4. Balkanbass mine, Kitchesta seam (Bulgaria); 5. Westerholt mine, President seam (F.R.G.). Hand-picked samples, with a high vitrinite content, were ground to pass a 0.02 mm sieve, treated with 8% HCl to decrease mineral matter below 5 wt. % and then prepared as described elsewhere². Data showing the petrographic content, ultimate and proximate analyses are given in Table I.

Reductive alkylation was performed after Lazarov and coworkers.² Directly prepared potassium-coal adducts were dispersed in dry THF and treated with 1-butyl iodide (BuI) (Fluka). The characteristics of benzene-soluble portions of reductively butylated coals (E1 through E5) are presented in Table II. The number of introduced alkyl substituents was calculated on the basis of atomic H/C ratio change caused by the reaction¹⁶.

About one gram of extracts E1–E5 was subjected to chromatographic separation on a silica gel column (Kieselgel 0.05–0.2 mm, Merck, 3 × 50 cm) using n-hexane, n-hexane–benzene (4 : 1 vol.), benzene, diethyl ether, and THF as eluents. Fractions of 50 ml each were collected and concentrated at reduced pressure. Elution by every eluent was gravimetrically measured.

TABLE I
Characteristics of the coal used

Property	Content in the coal, wt. %				
	1	2	3	4	5
Vitrinite	87	90	70	67	92
Ash	1.52	0.56	2.70	3.90	5.00
VM, maf	30.60	30.05	19.88	22.78	21.20
Element, maf					
C	85.90	86.50	87.19	87.94	89.20
H	5.50	5.50	5.34	5.29	5.20
N	1.59	1.42	1.71	1.60	1.40
S	0.97	0.49	1.27	1.47	1.00
O _{diff}	6.04	6.09	4.49	3.70	3.20
Yield of reductive butylation	122	126	134	118	137

TABLE II
Characteristics of benzene soluble portion of reductively alkylated bituminous coals

Value of	Benzene extract				
	E1	E2	E3	E4	E5
Yield, wt. % maf ^a					
	30	42	78	50	65
Element, wt. % maf					
C	84.94	87.00	86.16	87.81	87.82
H	7.74	8.45	8.47	8.05	8.90
Bu/100 carbon atoms ^b					
	6.9	9.5	10.5	8.3	13.4
\bar{M}_n	1 500	1 840	1 900	2 150	2 140
\bar{M}_n , corr ^c	1 030	1 100	1 070	1 350	970

^a Solubility of initial coal in benzene is c. 1 wt. %. ^b Calculated on the ground of atomic H/C ratio change, caused by the reaction. ^c Corrected for the number of butyl groups added.

Further hexane-eluted fractions (E1/1 to E5/1) were separated by preparative TLC on DC-Kieselgel 60 (Merck, 10 × 20 cm, 0.25 cm) in isooctane-THF (4 : 1 vol.) system, after Artz and Schweighardt¹⁷. Zones with $R_f = 1$ were scraped, hexane extracted and loaded on a small column (1 × 10 cm) containing an impregnated adsorbent (silica gel/10 wt. % AgNO_3). Normal alkanes were obtained by molecular sieve 5 Å (2 mm, Merck) adsorption after Selucky and co-workers¹⁸. Alkanes were investigated by GLC using Shimadzu instrument, 3% SE-30, 1 100 × 3 mm column, 100–300°C programmed, 10°C/min, Gas-Chrom Q (100–120 mesh), silanized, equipped with FID.

Aromatic fractions 2 of extracts were loaded on a $\text{SiO}_2/\text{Al}_2\text{O}_3$ column, using sample: adsorbent ratio 1 : 200 (wt.) and fractionated according to Hirsch¹⁹.

Acid-base fractionation was conducted as follows²⁰: Four grams of E5 were dissolved in benzene (1 : 10 wt.), cooled *n*-pentane was added (1 : 30 vol.) and precipitation of asphaltenes continued for 12 h. Then the insoluble portion was filtered, the filtercake was washed and dried in vacuum at 60°C. Soluble part (maltene) was concentrated in a vacuum evaporator and dried to a constant weight. The asphaltenes were fractionated in basic and acidic/neutral parts after Sternberg²⁰. Asphaltenes were dissolved in benzene (1 : 10 wt.) and dry HCl gas was bubbled through the solution. The bases formed insoluble adducts. They were removed by filtration, neutralized by a 10 wt. % NaOH solution and washed to neutral reaction. The Claisen alkali reagent, according to Husack and Columbic²¹, was employed to separate acidic and neutral portions.

The IR spectra of the fractions 3 to 5 of extracts were measured¹ in the KBr pellets (1 : 150 wt.) using Specord 75 IR spectrometer (Zeiss, Jena).

The ¹H NMR spectra were scanned on a Varian XL-100 instrument at 37°C: 10 wt. % solutions in C_2HCl_3 (Merck) were measured; tetramethylsilane (TMS) was used as internal standard. Chemical shift was in the δ scale. The hydrogen atoms in NMR spectra were classified as follows: the hydrogen attached to an aromatic carbon, H_{ar} , 9–6 ppm; the hydrogen attached to an α carbon to an aromatic ring, H_α , 4–2 ppm; the hydrogen contained in a methylene group at other than α position, H_β , 2–1 ppm; the hydrogen contained in a terminal methyl group, H_γ , 1–0.5 ppm.

Vapour phase osmometer (VPO) was employed for the determination of the average molecular weight, \bar{M}_n , in benzene and THF. The measurement was carried out at 45°C on a Knauer instrument calibrated with benzil. The samples were measured at three concentrations (4–15 g/l) and evaluated by extrapolation to infinite dilution.

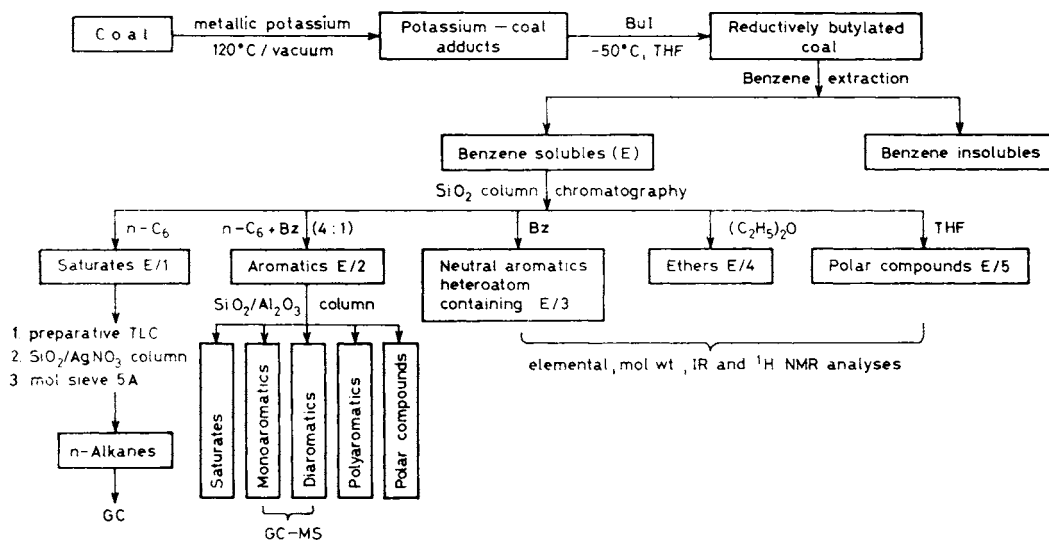
Average structural parameters of benzene, diethyl ether and THF eluted fractions were calculated according to Brown and Ladner²²: f_a , the aromaticity, ratio of the number of aromatic atoms to the total number of carbon atoms; σ , the degree of substitution of aromatic systems; $\text{H}_{\text{aru}}/\text{C}_{\text{ar}}$, the ratio of the number of aromatic hydrogen atoms to the number of aromatic carbon atoms for hypothetical unsubstituted aromatic system. This parameter and C_{AS} connected with it served to degree of condensation. C_{AS} is the average number of aromatic carbon atoms per structural unit (USW); n is the average number of carbon atoms per alkyl substituent (see ref. 23).

An alternative way to calculate the USW values from ¹H NMR data was suggested (see ref. 24). The number of structural units would be \bar{M}_n/USW , respectively.

RESULTS

Scheme 1 illustrates preparation, fractionation, and methods of characterization of benzene-soluble portion of reductively butylated coals. Data on the characterization

of E1 – E5 fractions are listed in Table II. The increase of yield is particularly pronounced in the case of E3 through E5. The yields of extractable material from untreated coals were trace and <2 wt. %, respectively, predominantly consisting of alkanes. Data from column chromatographic separations were summarized



SCHEME 1

in Tables III through V. The results given in Table III show that the degree of irreversible adsorption is low and it decreases with the rank of coals. The content of the first eluate was the lowest (1 to 3 wt. %), followed by that of aromatic fractions 2 of 9–14 wt. %. Due to their low quantity, elemental compositions were not measured and they (E1/2–E5/2) were subjected to column chromatographic fractionation (Table IV) and GC-MS investigations.

Fig. 1 presents the results from GC studies of n-alkanes (E1/1 – E5/1). Homologous series of C_{15} through C_{36} members were detected by comparing the retention times of the standard mixtures. The odd to even ratio (total sum of the content of alkanes with odd number of carbon atoms to that with an even number) were close to one, typical of coals from this coalification rank: E1/1 1.07, E2/1 0.97, E3/1 0.95, E4/1 0.96, and E5/1 0.92. The C_{23} through C_{26} members were most abundant.

The distribution of alkanes E4/1 and E5/1 have followed a bimodal pattern. The contents of lower alkanes C_{15} – C_{20} marked a relative increase with the increase in the rank, while in the case of E1/1 to E3/1, a negligible participation of the same members was detected (total sum of C_{15} – C_{20} about 10 wt. % of whole alkane

fraction), their contents sharply grew at E4/1 17 wt. % and the sum reached 28 wt. % at E5/1.

The data on fractionation of aromatic eluates (E1/2 to E5/2) on a dual packed $\text{SiO}_2/\text{Al}_2\text{O}_3$ column are given in Table IV. The saturates amounted to 10–12 wt. % that is 1 wt. % for the benzene-soluble portion of reductively butylated coal. With the increase in coal rank, a decrease in the mono- and diaromatic contents is observed. These fractions were mass-spectrometrically studied by electron impact technique of ionization (70 eV). Binaphthalene, benzothiazole, methylcarbazole, and butylthiophene were identified. There were mass spectral indications for 4–6 cyclic mono-

TABLE III
Balance of column chromatographic separation

Fraction	Eluent	Sample and extraction yield, wt. %				
		E1	E2	E3	E4	E5
1	n-hexane	1.3	3.1	1.0	1.3	1.7
2	n-hexane-benzene (4 : 1 vol.)	13.8	9.1	10.9	9.0	14.0
3	benzene	23.1	22.2	29.7	35.2	46.0
4	diethyl ether	50.0	38.4	25.5	28.0	29.5
5	tetrahydrofuran	1.1	21.7	30.1	25.5	7.6
Total		89.3	94.5	97.2	99.0	98.8

TABLE IV
Separation of aromatic fraction 2

Major components	Sub-fraction of aromatic fraction 2, wt. %				
	E1/2	E2/2	E3/2	E4/2	E5/2
Saturates	10.7	10.8	12.7	10.0	12.9
Monoaromatics	8.7	6.6	18.5	—	6.0
Diaromatics	17.9	4.4	21.2	21.7	6.4
Polyaromatics	30.0	50.0	26.6	24.3	17.9
Polar compounds	26.4	18.1	16.6	36.0	54.2
Total	93.7	90.0	95.6	92.0	97.4

butyl hydroaromatic compounds from Z-series: -14, -16, -22, -24, -26, -28; with a molecular mass in the 300–360 amu range²⁵.

A dependence of the composition of the eluates on the carbon content of initial coals is evident from Tables III and V. With an increase in C, an upward tendency for aromatic fractions (E1/3–E5/3) is noticed (from 23.1 to 46.0 wt. %, see Table III). Diethyl ether eluted amounts (E1/4 through E5/4) decrease to sample E3, then remain unchanged (about 25–30 wt. %). A maxima for polyfunctional components (E1/5 to E5/5) is distinguished for E3 (30.1 wt. %).

The IR spectra measured are typical of coal extracts. The increase in the aliphatic region is particularly pronounced, due to the introduction of alkyl substituents. Prominent bands appear at 2 860, 2 930, 1 470, 1 380 cm^{-1} and are assigned to CH_2 and CH_3 groups. The strong vibrations of the CH_2 and CH_3 groups of butyl groups are located at 2 930 and 2 860 cm^{-1} , and the asymmetric methyl appears as a shoulder at 2 950 cm^{-1} . The band at 1 460 cm^{-1} is due to either asymmetric $\text{C}-\text{CH}_3$ or CH_3 , whereas the band at 1 380 cm^{-1} is due to a symmetric $\text{C}-\text{CH}_3$.

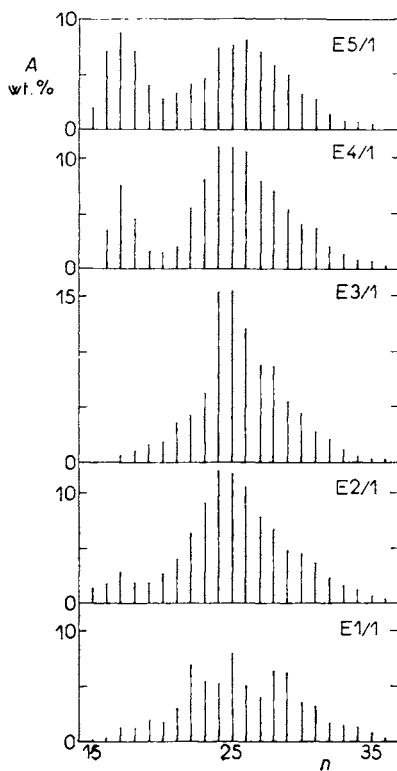


FIG. 1
Pattern of n-alkane distribution. A Content of n-alkane (wt. %), n number of carbon atoms

TABLE V
Characteristics of the sub-fractions 3 through 5

Sub-fraction	Element, wt. %		\bar{M}_n
	C	H	
E1/3	82.20	8.19	1 000
E1/4	82.61	7.52	1 950
E2/3	85.97	8.27	2 500
E2/4	85.39	8.50	1 430
E2/5	79.51	8.47	880
E3/3	85.68	7.46	2 650
E3/3	85.64	8.02	1 950
E3/5	83.39	7.80	1 720
E4/3	88.39	8.06	2 200
E4/4	86.08	7.73	1 950
E4/5	82.03	8.30	880
E5/3	86.82	9.70	2 200
E5/4	85.00	8.33	2 100

TABLE VI
Distributions of the protons in the ^1H NMR spectra

Sub-fraction	Protons			
	H_{ar}	H_x	H_β	H_γ
E1/3	0.187	0.240	0.373	0.200
E1/4	0.137	0.275	0.263	0.226
E1/5	0.093	0.279	0.450	0.178
E2/3	0.227	0.201		0.571
E2/4	0.157	0.131	0.437	0.275
E2/5	0.224	0.200	0.291	0.286
E3/3	0.200	0.206	0.271	0.324
E3/4	0.188	0.208	0.285	0.319
E3/5	0.126	0.255		0.619
E4/3	0.243	0.185		0.573
E4/4	0.205	0.197		0.598
E4/5	0.153	0.240	0.459	0.148
E5/3	0.158	0.187	0.276	0.335
E5/4	0.165	0.196	0.351	0.289
E5/5	0.105	0.105	0.553	0.237

The band at $1\,600\text{--}1\,610\text{ cm}^{-1}$ represents conjugated C=C bonds. The bands at $3\,030\text{ cm}^{-1}$ represent aromatic C—H stretching.

The spectra of benzene eluates do not have bands for oxygen containing functional groups: strong, almost equally spaced bands at 865 , 815 , and 750 cm^{-1} are noticed, representing aromatic out-of-plane frequencies of aromatic structures. The last one at 720 cm^{-1} is usually attributed to alkyl substituent $(\text{CH}_2)_n$, where $n = 4$. A band at $3\,460\text{ cm}^{-1}$ is considered as hydrogen in pyrrole.

In the diethyl ether and THF eluates bands at $1\,080$, $1\,250$, and $1\,720\text{ cm}^{-1}$ are found and related to ether and carbonyl groups.

The distribution of hydrogen atoms from ^1H NMR spectra of the benzene, diethyl ether, and THF fractions are given in Table VI. The preponderance of hydrogen in aliphatic structures should be stressed. A low value for H_{ar} has been checked. In Table VII are summarized the average structural parameters calculated.

The values of f_a fall in a relatively broad range (0.44 up to 0.61) and, in contrast, of H_{aru}/C_{ar} in a narrow one (0.60 up to 0.72), corresponding to a hypothetical aromatic system of $4\text{--}5$ rings. The content of C_{ar} is about 16 atoms for benzene fractions, corresponding to a value for 4 cyclic condensed aromatic hydrocarbons. The values for n are $3.1\text{--}4.8$ which coincide roughly to the length of the alkyl group added and confirm the validity of the calculation method. The data on *USW* cover the interval $320\text{--}450$ amu (excluding the highest and lowest data). The number of elemental structural units is the highest for benzene eluates.

Results from fractionation of the benzene-soluble portion of E5 in a manner borrowed from the investigation of petroleum heavy ends, are presented in Table VIII. One is impressed of the very high molecular weight measured for basic fraction ($<6\,000$ amu). In our opinion such value cannot be considered as meaningful because of probable high degree of association. The \bar{M}_n is low for the maltene fraction. In Table VIII no enrichment with nitrogen in material adducted by HCl could be achieved, only chlorine remains chemically bonded as a result of the treatment (c. 2 wt. %). The attempts to dissolve completely the basic components in organic solvents were unsuccessful (30 wt. % solubility in benzene, 70 wt. % in THF); similar results have been reported by Bockrath²⁶. E5 behaviour is due to the replacement of active H atoms, the functionality is obscured and, consequently, there is little effect from treatment with acidic and basic reagents; hence, this manner of fractionation of the soluble product by HCl-adduction cannot be regarded as suitable in the case of reductively alkylated coals.

DISCUSSION

Reductive alkylation is connected with a variety of reactions²⁷ — reductive alkylation of aromatic system (resulting in C-alkylation), cleavage of the ether linkage between the various structural fragments and alkylation of phenolic groups (resulting

in O-alkylation). There are indications for the abstraction of protons, rupture of thioether bonds and labile C—C bonds (*e.g.* in polyarylethanes), and alkylation of nitrogen nucleophilic atoms. The addition of alkyl groups resulted in suppressing

TABLE VII
Average structural parameters of the sub-fraction 3 through 5

Sub-fraction	Structural parameter						
	f_a	σ	$H_{\text{aru}}/C_{\text{ar}}$	C_{AS}	USW	n	\overline{M}_n/USW
E1/3	0.51	0.51	0.88	8.0	230	3.1	4.4
E1/4	0.53	0.62	0.74	11.8	320	3.7	6.1
E2/3	0.58	0.31	0.61	17.8	400	3.4	6.3
E2/4	0.51	0.41	0.61	17.8	490	4.8	2.9
E2/5	0.57	0.31	0.63	16.6	380	3.4	2.3
E3/3	0.61	0.34	0.48	29.4	630	3.4	4.2
E3/4	0.54	0.45	0.71	12.9	340	3.4	5.7
E3/5	0.51	0.39	0.71	12.9	360	3.4	4.8
E4/3	0.60	0.28	0.59	19.1	420	3.6	5.2
E4/4	0.57	0.58	0.67	14.6	380	3.5	5.4
E4/5	0.55	0.65	0.71	12.9	340	3.3	2.6
E5/3	0.44	0.42	0.84	8.9	280	3.7	7.9
E5/4	0.51	0.46	0.72	12.5	350	3.8	6.0

TABLE VIII
Acid-base fractionation of E5 sample

Fraction	Content wt. %	\overline{M}_n	Elemental composition, wt. %				
			C	H	N	S	O _{diff}
Maltene	30.0	750	86.47	8.10	0.95	2.00	2.48
Asphaltene	66.0	3 450	86.77	7.22	1.00	0.73	4.28
Asphaltene, basic ^a	28.4	6 000	83.60	8.65	0.85	0.96	4.76 ^b
neutral + acidic ^a	29.7	2 120	86.16	8.32	1.04	1.80	2.40
neutral ^a	27.6	2 200	86.40	8.40	1.00	1.10	3.10
acidic ^a	<1.0						

^a Calculated on the whole E5 sample. ^b Chlorine content of 1.18 wt. %.

the donor-acceptor interactions and in splitting large fragments from the coal structure; further, it considerably affected the coal spatial organization. The advantages of this approach are the relatively mild treatment and the absence of conditions for large structural rearrangements.

One is compelled to conclude that benzene eluates contained predominantly C-alkylation products, as indicated by high values of f_a , low σ , and a relatively high number of "stacked" aromatic layers (\bar{M}_n/USW) for these fractions. The assumption is confirmed by the IR data, lacking the bands of oxygen containing functional groups. Following the content of benzene eluates as a function of the raw coal carbon content, one is impressed by the fact that at 87% C content aromatic structures reach a significant degree. The associations on the basis of $\pi-\pi$ interactions (about 5-7 aromatic stacks) should not be excluded. These fragments acquire a high solubility in organic solvents after alkylation.

It may be assumed that in the diethyl ether and THF eluates O-alkylation products are concentrated, an assumption which is supported by the IR data and proton distribution.

The C-alkylation to O-alkylation ratio (the ratio of the yields of the benzene to diethyl ether + THF eluates, respectively) is traced out as a function of C content of initial coals in Fig. 2. An increase in the C-alkylation behind 87% C region is observed. High values for C_{ar} , \bar{M}_n/USW , f_a were calculated, USW increases and all these parameters have their maxima at 87% C.

It is known that anthracite is not amenable to alkylation under such conditions^{23, 28, 29}. A possible explanation for this fact is a lack (negligible or hindered content) of oxygen which does not allow the O-alkylation.

It may be supposed that the process of alkylation starts with an attack on the oxygen functions (predominantly ethereal bridges) resulting in the destruction of the "super" macromolecular coal structure and its breaking into large pieces. Then C-alkylation preponderance begins to play the important part. When the aromatic

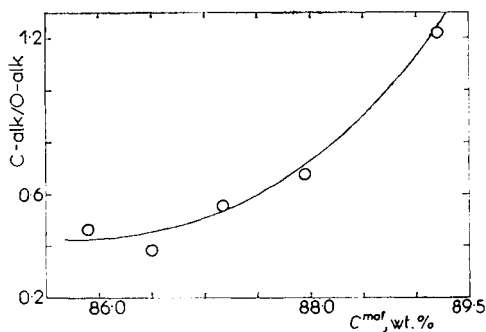


FIG. 2
Ratio of C-alkylation to O-alkylation vs
carbon content of initial coal C^{maf} , wt. %

system of π electrons is conjugated in an enormous aromatic hydrocarbon and the heteroatoms in acidic and neutral functions are present in negligible amounts, there is a weak possibility for a labilization of the aromatic system due to cleavage of bonds, and as a result, anthracite is not amenable to alkylation.

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