

### 3. Model Compounds

#### A. Hydrocarbon Ring Structures

1973

3.1 138597s Spin excitations of bitumens. Yen, T. F.; Young, D. K. (Dep. Med., Univ. South. California, Los Angeles, Calif.). Carbon 1973, 11(1), 33-41 (Eng). Bitumen free radicals are located within the planar polynuclear aromatic ring systems of bituminous crystallites in such a manner as to optimize their stabilization by the resonance of delocalized  $\pi$ -electrons. The states of spin multiplicity of these substances are shown by the transitions during thermal excitation. Exptl. ESR intensity-temp. dependence data from several asphaltic bitumens, a model compd. (phthalocyanine), and a few charge-transfer complexes were collected. Curves contg. both exponential (singlet-triplet) and Curie-Weiss (doublet) components were then calcd. and found to be consistent with published results. This spin correlation indicates that both single-triplet transitions and double states exist within the bituminous arom. sheets. This and other forms of thermal excitation, e.g. the Russell effect, are attributed to the propagation of Wannier excitons. The predominance of doublet concns. in high-V samples, e.g., Mara asphaltene, indicates that spins are localized by nuclei-spin interactions.

3.2 94542j Determination of the reaction kinetics parameters of coal oxidation. Lenart, L.; Abel, O. (Inst. Chem. Technol. Brennstofftech., Tech. Univ. Clausthal, Clausthal, Ger.). J. Therm. Anal. 1973, 5(2), 341-51 (Ger). The processes during the dry oxidn. of coal by gaseous O below 150° are discussed in terms of a connection between reaction and transport kinetics. A general model is proposed that includes the previously developed models which cover only discrete phases of the whole oxidn. range. The model therefore is utilizable for the whole range of coal oxidn. at low temps. It can be used to approx. the O-intake as a function of oxidn. time with oxidn. temp. or grain size as parameter. The selectivity of the oxidn. at different temps formally appears to be a result of the different activation energies of the coal oxidn. reaction consts.

3.3 7766u Effects of colloidal structure on physical measurements on coals. Evans, David G. (Dep. Chem. Eng. Univ. Melbourne, Parkville, Aust.). Fuel 1973, 52(2), 155-6 (Eng). Colloidal systems within org. and carbonaceous substances are precisely defined and the consequences of changes thereby

indicated. Distribution of porosity in a brown coal is estd. This work may explain the apparent absence in lignites of capillaries with diam. between 1.2 and 30 nm, in terms of differences in colloidal structure between brown and black coals.

## 1972

3.4 149591m Mechanism of high-pressure coal hydro-genolysis of Taiheiyo coal. Maekawa, Yousuke; Ishii, Tadao; Takeya, Gen (Gov. Ind. Dev. Lab., Hokkaido, Japan). Nenryo Kyokai-Shi 1972, 51(12), 1233-41 (Japan). The structural parameters of the solvent-sol. fractions obtained by hydrocracking at 220-30 kg/cm<sup>2</sup> and 400° of Taiheiyo coal were detd. to deduce the chem. structure of the original coal and the hydro-cracking mechanism. Based on the exptl. results, it was suggested that the Taiheiyo coal may contain some 3-dimensional bonds.

3.5 18699e Bakelite as a structural model of coal. Loewenberg, Peter (Inst. Quim., Univ. Fed. Rio Grande de Sul, Porto Alegre, Brazil). Rev. Brasil. Tecnol. 1972, 3(3), 87-93 (Eng). There are many chem. and phys. analogies between coal vitrain and PhOH-HCHO resins. Coal appears to be a complex mixt. of PhOH-HCHO type plastics at various stages of condensation and polymn. The d., sp. heat, dielec. const., n, fusibility, pyrolysis behavior, ion-exchange properties of sulfonated samples, oxidative degrdn., release of HCHO in acid hydrolysis, and ir spectra all show close similarity between coal and phenolic resins.

3.6 61633z Smaller molecules. Overlooked component of coal. Vahrman, Mark (Dep. Chem., Univ. Dar es Salaam, Dar es Salaam, Tanzania). Chem. Brit. 1972, 8(1), 16-22 (Eng). Coal tars come from that portion of the coal having mols. of mol.wt. < 1000. They are present in the vitrinite and exinite group of macerals and in the inertinite group. The mols. of mol. wt. < 500 form a much larger proportion of the coal structure than previously thought and are the main precursors of tar.

## 1971

3.7 22600n Fractionation of a benzene extract of Yubari coal. I. Fractionation of the 265 to 316°-0.3 torr fraction. I. Imuta, Kazutoshi; Ouchi, Kohi; Kurihara, Koji (Natl. Res. Inst. Pollut. Resour., Japan). Nenryo Kyokai-Shi 1971, 50(12), 880-6 (Japan). The title fraction of the petroleum ether-sol. ext. was fractionated by liq. chromatog. on an Al<sub>2</sub>O<sub>3</sub> column. 1,2,3,4-Tetrahydro-2,2,9-trimethylpicene (I), monomethylpicene (presumably 2-methylpicene), 2,9-dimethylpicene, and trimethylpicene were found in crystals sepd. from the 2nd to 9th fractions.

1969

3.8 41084q Molecular structure of coal. Oelert, Henning H. (Tech. Univ. Clausthal, Clausthal-Zellerfeld, Ger.). Brennst.-Chem. 1969, 50(6), 178-82 (Ger.). The  $\text{CHCl}_3$ -sol. part of pyridine exts. from 3 Ruhr coal samples (23.5-34.5% volatile matter) was sepd. by gel chromatog. on a Sephadex LH-20 column (1100 x 18 mm.). Detn. of mol. wts. gave distribution curves with max. in the 350-500 range. N.M.R. and ir data supported the view that coals with >28% volatiles are made up of smaller aromatic structural units, whereas in older coals, peri-condensed systems predominate.

3.9 116952m Controlled degradation of coal and its derivatives by hydrogenation. Comparative study of model compounds. Develotte, J.; Mazza, M.; Payen, P. (Centre Etudes Rech., Charbonnages de France, Fr.). Bull. Soc. Chim. Fr. 1969, (1), 341-8 (Fr). Various types of coal (exinites and vitrinites) and pitch together with model substances were hydrogenated in a glass app. by using  $\text{MoS}_2$  as catalyst from 340 to 430° at 0.1-10 torr. Analyses of the products of hydrogenation of coal, pitch, and model substances are compared. Dibenzoylaminodanthrimide, 1, 1'-Bi-2-naphthol, dodecylpyrene, dimethoxydibenzanthrone, pyranthrone, and a phenol-HCHO resin were the model substances evaluated. Hydrogenation products of coal and pitch consisted of condensed cyclic and polycyclic hydrocarbons contg. 30-48 C atoms. These substances corresponded to the products obtained from by hydrogenation of model substances having mainly a pyrene structure.

1966

3.10 A comparative study of exinite, vitrinite, and micrinite. H. Tschamler and E. De Ruiter (Union Carbide European Res. Assoc. S.A., Brussels, Belg.). Advan. Chem. Ser. No. 55, 332-41, discussion 342-3 (1966) (Eng). An exinite, vitrinite, and micrinite of the same rank were investigated. From elementary analysis alone, it follows that their structures must be different. Combining the results from ir and proton-spin resonance measurements, the H distribution, the aliphatic-group distribution, and possible intervals for the aromaticity are derived. Exinite has the highest relative amt. of  $\text{CH}_2$  groups and micrinite has the lowest amt. From x-ray measurements and H distribution, limits for the aromatic cluster size are derived; exinite has the least clusters, micrinite the most. Finally, the presence of nonaromatic rings is demonstrated, of which at least a part should be hydroaromatic or alicyclic.

3.11 The function of solvent extraction products in the coking process. II. A theory of the mechanism of thermal softening. H. R. Brown and P. L. Waters (C.S.I.R.O., Div. Coal Res., Chatswood, New South Wales). Fuel 45(1), 41-59 (1966) (Eng); cf. preceding abstr. Thermal softening is explained in terms of a "mixed isogel" model that supposes vitrinite to consist of (A) fusible  $\text{CHCl}_3$ -sol. "bitumen" mols, as the dispersion medium, and (B) infusible "humic" micelles dispersible in pyridine as the dispersed phase. In the solid state, the micelles of B are held together by van der Waals forces as a rigid gel with mols. of A included in the pores of this matrix. Initial thermal softening ( $\sim 350^\circ$ ) is believed to be essentially a thermophys. process of gel/sol transition, but fluidity is subsequently modified by thermochem. and mech. processes, which are explained in detail. The extn. products A and B are probably derived from different coal-forming plant chemicals along different metamorphic tracks and bear a generic relation to certain petrographic components. Both m.ps. and decompn. temps. of extn. products are functions of chem. compn. The conditions of softening are detd. by the relative proportions of fusible, colloiddally dispersible, and nondispersible components, and by the chem. compn. of these components. 139 references.

### 1965

3.12 Constitution and structure of Jiawang vitrinites by mild hydrogenation. II. Thin-layer chromatography of aromatic hydrocarbons and mild hydrogenation products from vitrinites. Mei-Jen Shih, et al. Acta Foculio-Chim. Sinica 6(3), 250-8 (1965) (Ch); cf. CA 64, 19259a. Analysis of aromatic hydrocarbons and of the mild hydrogenation products of Jiawang vitrinites was made by alumina and silica-gel thin-layer chromatography. The retention data from the chromatograms indicated that the aromatic hydrocarbons were arranged according to the no. of aromatic rings, esp. the no. of double bonds including conjugated and nonconjugated bonds, so that it is possible to make use of the thin-layer chromatography as a method for group identification. From the chromatograms of the hydrogenation products and their aromatic fractions of Jiawang vitrinites, it was shown that biphenyl, biphenylmethane, and their derivs. were absent in the fractions of monocyclic aromatics. This has led to the conclusion that structural units with monocyclic aromatic and satd. naphthenic type are present in the original vitrinites, and they are not the products of hydrogenation of other structural units during mild hydrogenation. From Sci. Abstr. China, Chem. Chem. Technol. 4(1), 24 (1966).

1964

3.13 Physical and chemical properties of hard coal components. XVI. The influence of the degree of coalification and of the process rate on the results of pyrolysis in high vacuum. Carl Kroeger and Peter Unrath (Tech. Hochschule, Aachen, Ger.). Brennstoff Chem. 45(1), 9-15 (1964). Vitrinite, micrinite/semifusinite, and exinite of Ruhr coal beds, as well as vitrinite of the Wilhelm bed, were subjected to high-vacuum breakdown at 525°. Yields of coke, tar, water, and gases were detd. and the gases analyzed for H, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, butane, butene, CO, and CO<sub>2</sub>. In comparison with the step-wise high-vacuum pyrolysis described in previous work, considerably higher tar and lower gas yields were obtained in the direct approach. Direct pyrolysis is the least destructive of the two methods in terms of "bitumen" yield. A theory, making use of a cell-structure concept, is developed to explain this. It was possible to correlate the wax-resin content of the coal (the bitumen formers) with the tar yield and also with the yield of certain gaseous hydrocarbons.

1963

3.14 Composition of a low-temperature bituminous coal tar. Howard W. Wainwright (Bureau of Mines, Morgantown, W. Va.). Am. Chem. Soc., Div. Fuel Chem., Preprints 7(1), 143-68 (1963). This paper summarizes the separatory and qual. and quant. procedures for characterizing a low-temp. bituminous coal tar. These include microvacuum fractional distn., infrared and ultraviolet spectrophotometry, gas-liquid and displacement chromatography, and countercurrent distribution. In the distillate fraction b.  $\leq 350^\circ$ , approx. 130 individual compds. were identified among the tar acids and bases, 95 among the aromatic hydrocarbons and 21 among the C<sub>10-16</sub> hydrocarbons, 7 each of normal paraffins, 2-methyl alkanes, and  $\alpha$ -olefins. These were identified mostly with respect to individual isomers, and the amts. were detd. or estd. in nearly all instances. The resins from the pitch of lignite, subbituminous, and bituminous low-temp. tars were characterized by ring analysis, infrared and ultraviolet spectra, and by combined pyrolysis and gas-liquid chromatography. The resins contained isolated benzene rings joined together by satd., fused, multiring systems with satd. bridge carbons, including quaternary carbons.

3.15 Chemicals from coal hydrogenation products. M. D. Schlesinger (Bur. of Mines, Pittsburgh, Pa.). Am. Chem. Soc., Div. Fuel Chem., Preprints 7(1), 184-93 (1963). A large quantity of chemicals are now made from coal by carbonization. The supply could be increased significantly by products from the hydrogenation of coal but not necessarily at competitive prices.

A no. of high-mol.-wt. compds. can be sepd. from the products of coal hydrogenation, but large-vol. markets do not exist as they do for the lower-mol.-wt. compds. Recent research at the Bureau of Mines has produced gaseous hydrocarbons by the hydrogenation of dry coal. From this research came the synthesis of coronene by the hydrogenation of anthracite. Also, a mixt. of closely related chemicals produced from coal by hydrogenation has been hydrogenated to a jet fuel that may be suitable for supersonic aircraft.

3.16 Test of hydrogenation of a coal by atomic hydrogen. Maurice Letort, Andre F. Boyer, and Pierre Payen. Bull. Soc. Chim. France 1963(8-9), 1589-93. Atomic H, obtained in 20-50% concn. by elec. discharge in H at 0.4-0.7 mm., completely reduced C and coronene to  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$ . But paraffins, phenanthrene, and pyrene under the same conditions left a high-mol.-wt. residue contg. hydrogenated aromatic structures. Vitrinite (I), a sample of coal contg. 84.5% C and 8.2% O, left only its inorg. residue, and a pyridine ext. of I left no residue upon hydrogenation. The reaction velocities were increased by the presence of 3%  $\text{H}_2\text{O}$  in the H, but in that case, the gaseous products were mainly  $\text{CH}_4$  and CO, in concns. which indicated that the reaction involved 1 mol.  $\text{H}_2\text{O}$  out of 15 and 1 atom H out of 500. Since the degradation of the coal by hydrogenation yielded only light gaseous products, it gave no information on the structure of the coal.

### 1962

3.17 Mechanisms of coal pyrolysis. V. Kinetics of pyrolytic dehydrogenation in the range 600° to 800°. N. Berkowitz, and W. den Hertog (Res. Council Alberta, Edmonton, Can.). Fuel 41, 507-20 (1962); cf CA 55, 22773b. Rates of H formation in the temp. range of 600-800° are reported for 3 coals of widely different rank. Between 35 and 70% of the total H available at any one temp. disengages with 1st-order kinetics, but the apparent activation energies calcd. from the corresponding rate consts. are low and vary from 8 to 15 kcal./mole. Since rate control by C-H bond rupture or gaseous diffusion must be ruled out, the rate-detg. step must be a function of lamellar mobility, i.e. H forms in a bimol. process which occurs whenever 2 contiguous C lamellae move into an appropriate configuration.

3.18 Self-consistency of statistical structural analyses [of coal, tar, and pitch]. Valerie Sandor, Ernest de Ruiter, and Hubert Tschamler (Union Carbide European Res. Assoc. S. A., Brussels, Belg.). Erdoel Kohle 15, 713-17 (1962). To det. the complex structures of coal, tar, and pitch, the use of a graphic densimetric method, reconstruction of ultraviolet and visible absorption, and aromatic-aliphatic H distribution

are discussed. The results of using these methods for detg. the aromaticity, ring condensation index, mean size of condensed aromatic systems, max. aromaticity, and aromatic substitution index are given for samples of tar and pitch. 12 references.

3.19 Origin of coal-tar pitch. E. W. Volkmann and C. C. Russell (Koppers Co. Inc., Pittsburgh, Pa.). Fuel 41, 535-9 (1962). The close similarity between many of the phys. and chem. properties of the vitrinites of high-rank, low-volatile, bituminous coals and of coal-tar pitches produced from high-temp. coal tar indicates that these substances contain some identical structural units. These units are probably derived from the vitrain fraction of the coal during carbonization and appear in the condensing tar after modification due to pyrolysis. High-temp. pyrolysis seems to bring about in sec. what nature accomplished in millions of years.

3.20 Determination of acene groups [anthracene structures] in hard coals. F. Micheel, J. Bernsmann, and G. Draeger (Univ. Muenster, Westf., Ger.). Brennstoff-Chem. 43, 49-50 (1962). The  $C_5H_5N$  and  $C_6H_6$ -insol. fractions (I) from each of 6 coals (C 84.35-91.59%) were refluxed with satd. xylene solns. of maleic anhydride. After conversion of the resulting endo-succinic anhydride derivs. to the acids (II) these and I were each methylated with diazomethane. The differences in the OMe contents of I and II indicated the % of acene groups in I. The content of the acene groups, calcd. as anthracene, decreased with increasing degree of coalification from 9.9% in gas coal to 1.0% in anthracite. Similar expts. with 2,3-dibromomaleic anhydride, in which the hydrolysis rates of the Br in the products were measured, confirmed these results. Expts. with HCHO copolymers with anthracene and phenanthrene showed that they contained 18.7 and 0.5% acene groups, resp.

3.21 Molecular motion and arrangement in coal by nuclear magnetic resonance methods. Y. Sanada and H. Honda (Resources Res. Inst., Kawaguchi, Saitama, Japan). Fuel 41, 437-41 (1962). Results obtained by the broadline n.m.r. method have a no. of implications with regard to the mol. motion and arrangement in the coal. Calcn. of the activation energy at near the glass temp. and the degree of crystallinity has been attempted. The values of activation energy are higher than those of synthetic high polymers and suggest a motion more hindered by strong mol. forces in the coal.

1961

3.22 Thermal stability of constituents of coal tar and their derivatives. Hajime Suzumura (Tokyo Lab. Res. Center).

Kogyo Kagaku Zasshi 64, 1978-83 (1961). In order to det. the thermal stabilities of the constituents of coal tar and their derivs. in relation to their chem. structures, aromatic hydrocarbons, aromatic ethers, F compds., and Si compds. were either synthesized or purified and were then heated in sealed tubes. Heating was conducted for various times at various temps., and the properties of the samples, such as color, m.p., absorption spectrum, and deposition of carbonaceous matter, were then examd. Also, the samples were heated in air to accelerate oxidative deterioration. Para-substituted biphenyls, such as p,p'-difluorobiphenyl, p-phenoxybiphenyl, terphenylene, and 1,3,5-triphenylbenzene, all having low free valency, were found to be thermally as stable as biphenyl and terphenyls. On the other hand, compds. such as bibenzyl which had chem. bonds of low dissocn. energy, were cracked considerably even after short periods of heating.

3.23 Changes in structure and properties of Kara-Kichia brown coal during thermal treatment. K. Usenbaev. Vestn. Akad. Nauk Kirg. SSR 1961, No. 1, 53-63. Samples of brown coal from northern mines of the Kirgiz S.S.R., contg. ash 8.6, moisture 12.5, and volatile material 37.4%, were subjected to thermal treatment at temps ranging from 1000° to 2800° in N. Structural changes occurring in the coal at various temps. were studied by x-ray diffraction, and detns. were made of the thermoelectromotive force (with respect to Cu) and of elec. cond. of the heated samples. A homogeneous transition from the amorphous structure to a graphitic cryst. network was observed, without coexistence of the phases. Crystn. began at 2200°, and its rate increased with temp. As compared with anthracite from the Donets Basin, the crystn. rate was considerably lower, and the lattice did not attain the perfection of that in native graphite. The x-ray diffraction pattern indicated that the structure of brown coal is intermediary between that of graphitizing materials (anthracite, petroleum coke) and nongraphitizing materials (channel black, sugar C).

3.24 Chemical constitution of the bituminous coal of Yubari. Tsutomu Sakabe. Shigen Gijutsu Shikensho Hokoku No. 49, 1-61 (1961) (Japan). Yubari coal is a typical Japanese coking coal. By treatment with H at 360-70° in the presence of a Cu-Ba-Cr accelerator, an oil was obtained which was sol. in petr. ether in a yield of 56.8% in relation to C balance. Of this oil (b<sub>2-3</sub> 315°), 77% consisted of 6.8% bases, 10.7% of acid oils, and 83% of neutral oil, from which 4.1% could be obtained with urea. The basic portion was sepd. into 4 fractions, mol. wts. 159-246, 58-86% tertiary amines. The content of the amines increased with increasing mol. wt., that of secondary amines decreased. The neutral oil yielded 13 fractions with a mol. wt. of 151-393, which were investigated after elimination of paraffin and dehydration on Pt. The content of



OH and basic N groups increased with increasing mol. wt. Also, the neutral oils contained inactive O and nonalk. N. The acid oil was sepd. into 5 fractions with a mol. wt. of 125-283 after methylation of the OH groups. The neutral oil fractions contained 1-4 aromatic rings/mol., which were catacondensed, with 53-63% aromatic C. Most of the methylated acid oils contained 1 benzene ring/mol. The petr. ether ext. of the coal was a viscous oil. From this oil, small amts. of 4,11-dimethylpicene were obtained. Solid bitumen and pseudobitumen, obtained by pressure extrn. in  $C_6H_6$  and subsequently hydrated under mild conditions, were sepd. with ligroine, MeOH, ether, acetone, and  $CCl_4$  into 7 parts. The mol. wt. of these parts increased from 300 to 1400. All parts contained OH groups and groups with inactive O. Some contained a few CO groups. While eliminating the O and N groups, relations were found between the amt. of H/mole, the molar vol., the molar heat of combustion, and the no. of C atoms/mole of solid or pseudobitumen. With pyridine, ~4% ext. was obtained from the coal, and it was assumed that the mols. in soln. had a diam. of 10-20 Å. The Yubari coal had an av. compn. of  $C_{22}H_{24.3}N_{0.3}O_{1.6}$  and it contained 2.9 catacondensed aromatic rings/mol., in addn. to 8 aliphatic C atoms and 0.4 acetyltable OH groups. The ratio of aromatic C to total C varied greatly. Some of the aromatic rings were connected with each other and thus formed the coal mols., of which some had a diam. of 10-20 Å. A high content of H and of volatile substances produced an aromatic content of only 64%.

1959

3.25 Chemical nature of thermal decomposition and coke formation. V. E. Rakovskii. Khim. Pirogen. Protseessov, Inst. Torfa Akad. Nauk Belor ssk. SSR, Mosk. Torf. Inst. 1969, 165-84; cf. following abstr. The chemistry of coking and coke formation is discussed. Coke formation and caking resulting from the thermal treatment of low-mol. wt. compds. are condensation processes of aromatic compds., leading to the formation of high-mol.-wt. thermally-stable polynuclear aromatic compds. Caking consists of the substitution of  $C_6H_6$  rings by aromatic radicals. The coking process is most evident when heating aromatic hydrocarbons under pressure in the liquid phase. In the prepn. of biphenyl, it is necessary to use special catalysts that accelerate coke formation. Naphthalene, heated in an autoclave to 350°, is easily transformed into coke. Pyrolysis of aromatic compds. results to a slight extent in ring rupture, and the basic ring condensation process is accompanied by sepn. of a corresponding amt. of H. The reactivities of polynuclear compds. are not identical and depend on structure. Hydrogenation of aromatic compds. results in a decrease in stability of the compds. obtained. Cracking of Tetralin at 650° gives 75% naphthalene and, under the same conditions, Decalin gives 10% naphthalene,

10%  $C_6H_6$ , 10% PhMe, and about 50% low-mol.-wt.  $C_{1-5}$  hydrocarbons. If the high-mol.-wt. coal resin consists mostly of aromatic hydrocarbons, the solid fuel contains a large amt. of the corresponding cyclic unsatd. and satd. compds. of the naphthenic series. These unsatd. compds. are easily hydrogenated and converted to aromatic ompds. capable of giving stable condensation products. Mechanisms for these processes and for the formation of S- and N-contg. coke are proposed.

## B. Alkyl Substituents

### 1972

3.26 143272v Benzenecarboxylic acids obtained by the oxidation of Kuznetsk Basic coals by oxygen and air in an alkaline medium. Kukhareno, T. A. (USSR). Zh. Prikl. Khim. (Leningrad) 1972, 45(1), 172-5 (Russ). Most of the acids were identified and detd. by a gas-liq. chromatog. method and max. yields of the acids were reached at 270°. The yields of total and polycarboxylic acids were max. when fatty and lean coals, resp., were oxidized. Benzenetri- and benzenetetracarboxylic acids were the chief components. The weathered coals yielded more total and benzenepolycarboxylic acids in a single-stage oxidn. than the unweathered ones in a 2-stage oxidn., involving oxidn. of the coals with air during the 1st stage. 1,4-disubstitution is low or nil.

### 1970

3.27 122220z Oxidation of solid fuels with potassium permanganate in an alkaline medium as a method of coal structure investigation. Salbut, Piotr D.; Wielopolski, Aleksander (Inst. Chem. Org., Polska Akad. Nauk, Warsaw, Pol.). Roczn. Chem. 1970, 44(3), 585-601 (Ger). Structure parameters detd. in a series of solid fuels such as peat, brown coal, bituminous coal, anthracite coal, soot, and graphite, either by van Krevelen or Jurkiewicz and Zielinski methods, were found to be in a regular relation to yields of benzenecarboxylic acids (I) obtained by oxidn. of the fuel with  $KMnO_4$ . Conclusions were drawn concerning the coalification and chem. compn. of a particular kind of fuel. Except for terephthalic acid, the following I were isolated and detd.: benzoic, isophthalic, phthalic, 1,3,5-benzenetricarboxylic, 1,2,4-benzenetricarboxylic, 1,2,3-benzenetricarboxylic, 1,2,3,5-benzenetetracarboxylic, 1,2,4,5-benzenetetracarboxylic, 1,2,3,4-benzenetetracarboxylic, benzenepentacarboxylic, and benzenehexacarboxylic acid.

1966

3.28 Oxidation kinetics of coal. II. Gravimetric and volumetric experiments; change in calorific value and swelling index. Ehrenfried Schuett (Tech. Univ., Berlin). Erdoel Kohle 19(1), 32-8 (1966) (Ger); cf. CA 62, 6303d. The first attack of O upon coal involves aliphatic groups:  $:CH_2 + O_2 \rightarrow :CO + H_2O$ . This results in a wt. increase with formation of compds. of the humic acid type and removal of H. The second stage is the conversion of this product ( $C_6H_2O_2$ ) to  $CO_2$ , CO, and  $H_2O$ , and it continues until the org. matter is completely consumed. After drying and evacuation, coal sorbs O (or N) rapidly during the first few min. (adsorption); subsequently, O is consumed (chem. reaction) more slowly for many hrs. Relations involving wt. change of coal samples, consumption of O, pressure, and time are described graphically and math. The change in the calorific value of coal was small but increased rapidly during absorption of up to 5% O (detd. by difference), then remained fairly const. at  $140 \pm 10$  cal./g. The swelling index of a 0.1-0.2-mm. coal sample oxidized at  $150^\circ$  decreased from 8 to 1 in 10 hrs., while the wt. increased  $\sim 1\%$ ; this change was slower for oxidn. at lower temp. or with larger particle size.

3.29 Similar compositions of alkanes from coal, petroleum, natural gas, and Fischer-Tropsch product. R. A. Friedel and A. G. Sharkey, Jr. (U.S. Dept. of the Interior, Pittsburgh Coal Res. Center, Pittsburgh, Pa.). Advan. Chem. Ser. No. 55, 32-40, discussion 40-2 (1966) (Eng). Possible interrelations of natural substances are important. Similarities of the low-mol.-wt. alkane isomers from crude oil and Fischer-Tropsch synthesis product have been reported. A similar compn. for high-temp. coal carbonization has been found. The  $C_4$  to  $C_7$  alkane isomers from these sources can be calcd. quant. with equations developed for Fischer-Tropsch products. A reversal of the concns. of the monomethyl isomers from  $C_6$  (2 Me > 3 Me) to  $C_7$  (3 Me > 2 Me) occurs in all 3 products; comparisons at higher C nos. indicate some dissimilarities. Naphthene isomers for crude oil and high-temp. coal carbonization also have similar compns. Aliphatic hydrocarbons from low-temp. coal processes are considerably different. The  $^{13}C$  isotopic compn. of pure compds. from the various sources are being compared in order to provide information on their origin. 21 references.

1963

3.30 Studies in aerial oxidation. I. Oxidation of the vitrain from a bituminous coal. R. B. Conrow, R. A. Durie, J. S. Shannon, and S. Sternhell (Div. of Coal Res., C.S.I.R.O.,

Chatswood, Australia). Fuel 42, 275-90 (1963). Aerial oxidation of a vitrain of 82% C content at 170 and 190° was studied by chem. and infrared spectroscopic examn. of the solid products. The most important changes occurring during oxidn. are the virtual disappearance of aliphatic structures and the appearance of aromatic COOH groups; changes in the distribution of aromatic H, as manifested by infrared spectra, suggest that the aromatic portions of the coal structure are also changed during oxidn. No significant quantities of nonacidic CO groups were introduced, but some nonacetyltable OH groups appeared. The chemistry of aerial oxidn. of bituminous coals is more complex than much of the published information would suggest; however, the compn. of the alkali-sol. materials formed appears to be independent of the duration of oxidn. 48 references

3.31 The hydrogen distribution in macerals. W. R. Ladner and A. E. Stacey (Brit. Coal Util. Res. Assocn., Leatherhead, Engl.). Fuel 42, 75-83 (1963). Proton magnetic resonance measurements were made on a series of vitrinite, exinite, and fusinite concentrates of high purity. The results for the vitrinites and exinites are discussed in terms of H distribution and, by a combination of the n.m.r. data with those from infrared spectroscopy, the ratio of H in CH<sub>3</sub> + tertiary CH groups to that in CH<sub>2</sub> was calcd. This ratio lies between 0.7 and 1.0 for the exinites and between 1.0 and 1.4 for the vitrinites. Since the infrared spectra of these materials and other evidence indicate a low concn. of CH<sub>3</sub> groups, the proximity of the above ratio to unity indicates that an important fraction of the aliphatic H occurs in tertiary CH groups. Tentative estimates of the aromaticities of the fusinites were also made.

### 1959

3.32 Relation between chemical constitution and pyrolysis of coal. S. C. Biswas, S. Sarkar, K. A. Kini, N. N. Das Gupta, and A. Lahiri (Central Fuel Res. Inst., Jealgora). Proc. Symp. Nature Coal, Jealgora, India 1959, 261-5. Vitrains from high- and low-rank coals were carbonized at 1000° in a vacuum and the active O groups were characterized. A study of these active groups showed larger amts. of OH, CO, and COOH groups assocd. with the low-rank than with the high-rank coals. The higher amts. of CO and CO<sub>2</sub> evolved by the low-rank coal correlate with the higher contents of CO (and of ether) and of COOH groups, resp. in that coal. In conformity with the view that the no. of aliphatic side-chains is greater in low-rank coals, the amts. of CH<sub>4</sub> and other hydrocarbons evolved are greater with these coals. The C:H ratios of the residues, when plotted against the temp. of carbonization, showed that ring condensation occurs at about 500°.

## C. Sulfur Structures

1973

3.33 21450t X-ray photoelectron studies of sulfur in carbon. Harker, H.; Sherwood, P. M. A. (Chem. Dep. Univ. Newcastle-upon-Tyne, Newcastle-upon-Tyne, Engl.). Phil. Mag. 1973, 27(5), 1241-4 (Eng). X-ray photoelectron spectroscopy (ESCA) studies suggest that during the carbonization of sulfanilic acid, arom. ring systems contg. S may be formed and this is consistent with data obtained from model compds. contg. heterocyclic S. The conclusions are of interest in connection with the problem of S in coke.

1972

3.34 91026s Nature of coal extracts. III. Further progressive extraction and depolymerization of coal. Roy, Monmohan M.; Mitra, Sanjib K. (Geol. Surv. India, Calcutta, India). Erdoel Kohle, Erdgas, Petrochem. Brennst.-Chem. 1972, 25(6), 343-6 (Ger). The work described in CA 74: 89546f was continued to show that the no. of condensed rings is  $\leq 2$ , that the S is present mostly in heterocyclic structures, and that bonding between 2 units is mostly by CH<sub>2</sub> or heterocyclic structures.

1969

3.35 23250g Dissolving Karnatsaisk coals in organic solvents. Fisenko, N. N.; Larina, V. A.; Baranskii, A. D. (USSR), Vop. Khim. Khim. Tekhnol. 1969, 141-8 (Russ). From Ref. Zh., Geol., K. 1969, Abstr. No. 6K63. Results are given of a study of coal dissoln. in alc.-benzene (9 samples), pyridine (5 samples), and PhOH (8 samples). Data are given on the H<sub>2</sub>O and ash content in samples of natural and residual coals, on the yield of exts. and residual coals, and contents of various forms of S (total, sulfate, pyrite, org.) in natural and residual coals and exts. Pyridine and phenols not only transfer into soln. a part of the org. mass, but cause destruction of the coal macromols., part of the thio ether S being transferred into soln. The S atoms, which form thio ether groups, belong mostly not to the readily sol. part of the coal, but are bound directly to the main coal macromols.

1966

3.36 Pyrolysis of polycyclic compounds containing sulfur. P. X. Masciantonio and J. W. Walter (Appl. Res. Lab., U. S. Steel Corp., Monroeville, Pa.). Advan. Chem. Ser. No.

55, 687-94 (1966) (Eng). The pyrolysis of polycyclic compounds has been of considerable interest in studying carbonization and the manuf. of C products. It is usually desirable to minimize the S content of the carbonaceous residues resulting from pyrolysis of organic materials. To understand the disposition of S during pyrolysis, a series of model polycyclic sulfur-contg. compds. was pyrolyzed at 625°. The compds. were Ciba Pink B, Sulfur Black 2B, Hydron Blue G, Flavon GC, Alizarin Black B, Indanthrene Brown, Blue-Green FFB, Algol Orange RF, Ciba Orange R, and Cibanone Yellow R. A correlation between the S distribution and the elemental compn. of the compds. was observed. A mechanism of desulfurization that involves the probability of combining H and S atoms during pyrolysis appears to fit the exptl. data best. The study indicates that the volatile matter and O content of the model compds. are also significant factors in desulfurization.

#### 1961

3.37 Thio ether sulfur in some Irkutsk coals. V. A. Bogdanova and A. D. Baranskii. Kratkie Soobshch. o Nauchn.-Issled. Rabotakh za 1961 (Irkutsk: Irkutskii Univ.), Sb. 68 (Pub. 1963) (Russ). The chem. characteristics of org. bound S were studied in samples of coal from 4 deposits in the Irkutsk basin. Low-S Irkutsk coals had a high relative content of thioether groups ( $\leq 64.7\%$ ), while high-S coals were rich in org. bound S; these groups comprised  $< 10\%$  of the entire org. S in the coal. The bond between the org. S atoms in Irkutsk high-S coals and the central part of the coal macromol. was confirmed. From Ref. Zh., Khim. 1965, Abstr. No. 13P37.

3.38 Sulfur in the primary tars of certain Irkutsk coals. A. D. Baranskii, A. T. Zinina, and T. A. Toropova. Izv. Fiz.-Khim. Nauchn.-Issled. Inst. pri Irkutskom Univ. 5, No. 1, 36-42 (1961). Most of the S in Irkutsk coals enters into the gas or semicoke on coking. After semicoking of Zabitui, Delyursk, and Cheremkhovo coals, 3.6-6.5% of the total S content of the coal is found in the tar fractions b.  $\leq 325-60^\circ$ . In the 1st case, 78% of the S was found in high-mol.-wt., thermally stable compds. of the thiophene type. Cheremkhovo tar is characterized by a higher content of products of thermal decompn. of org. S compds. and a lower content (51%) of thiophene compds. From Ref. Zh., Khim. 1962, Abstr. No. 8M64.

#### 1958

3.39 Peculiarities in the behavior of sulfur from Irkutsk coal during fractionation of the latter with heavy

liquids. V. A. Larina, A. D. Baranski, W. N. Poljakowa, and N. F. Odinetz. Khim. i Tekhnol. Topliv i Masel 3, 36-43 (1958). Mineral coal discovered in various locations around Irkutsk was sepd. according to the method of Ammosoy (CA 47, 7188h) into fractions by  $C_6H_6-CCl_4$  mixts. of various d. to det. the content of total, mineral, and org. S and to establish the proportion of both varieties of S and total S. The liquid ds. were 1.40, 1.35, 1.30, 1.28, 1.26, 1.25, and 1.24, after which the fractions were simultaneously carbonized at low temp. or coked and then analyzed for S. The relatively const. distribution of total S in the coal mainly depended upon the org. S. The thermal decompn. of the latter did not reveal an isolated process, rather it was definitely connected with the simultaneously occurring decompn. of mineral S which resulted in the formation of  $H_2S$ , S, and S-contg. compds. Org. S was more completely decompd. if the coal contained little or no mineral S. The practical consequence of this finding is the necessity of removing mineral S before thermal processing of Irkutsk coal to obtain products low in S. From C.Z. 1960, 2736.

#### D. Oxygen Structures

1971

3.40 153640g Oxidation studies on coking coal related to weathering. II. Distribution of absorbed oxygen in the products resulting from the pyrolysis of slightly oxidizing coking coal. Ignasiak, B. S.; Clugston, D. M.; Montgomery, D. S. (Natl. Res. Counc. Canada, Ottawa, Ont.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1971, 14(1), 95-105 (Eng). A high-volatile A bituminous coal was oxidized 72 hr with  $^{18}O$  at  $100^\circ$  to simulate weathering, and subsequently pyrolyzed at various temps. to drive off  $Cl^{18}O_2$ ,  $Cl^{16}O^{18}O$ ,  $Cl^{18}O$ ,  $Cl^{16}O$ ,  $H_2^{18}O$ , and  $H_2^{16}O$ . These gases were analyzed by mass spectrometry and 60% of the  $^{18}O_2$  was in the tar + water fraction. The implication is that if mild weathering occurs, sufficient O crosslinks are introduced to have a profound influence on the phys. properties of the molten coal, such as the dilatation.

3.41 36007r Chromatographic study of alcohol-benzene extracts of some Bulgarian coals. Terebenina, A. V. (Inst. Neorg. Khim., Sofia, Bulg.). Khim. Tverd. Topl. 1971, (6), 40-5 (Russ). With increasing C content in coals, the amt. of neutral aromatic compds. increased in the  $EtOH-C_6H_6$  exts. The exts. from a Bulgarian lignite and 2 bituminous coals were examd. by liq. and gas-liq. chromatog., elementary anal., and

ir and uv spectroscopy. The liq. chromatog. of the part of the exts. sol. in petroleum ether took place in a column filled with a 1:1 silica gel- $\text{Al}_2\text{O}_3$  adsorbent at a 27:1 and 50:1 adsorbent-sample ratio. The eluents used were petroleum ether,  $\text{C}_6\text{H}_6$ ,  $\text{Et}_2\text{O}$ ,  $\text{EtOH}$ ,  $\text{Me}_2\text{CO}$ , and their mixts. In the aromatic part of the exts. from bituminous coals, acenaphthene, diphenyl oxide, 2,3-dimethylnaphthalene, and fluorene were identified by means of the Carlo Erba chromatograph. The ext. from the Maritsa-Iztok lignite was 56% sol. in petroleum ether and contained >90% O-contg. compds., including 27% acidic compds. and 60% neutral ethers, esters, and alcs. The ext. from Kachulka bituminous coal was sol. in an amt. of 58.2% in the petroleum ether and contained 0.5% paraffin-naphthenic compds., 19% alkylnaphthenes, and 16% phenanthrene-anthracene hydrocarbons. The ext. from Mazalaka bituminous coal was 75.6% sol. in petroleum ether and contained 50% neutral O-contg. compds., 40% aromatic compds., and 10% acidic compds.

### 1970

3.42 132778t Low-temperature oxidation of coals studied by ir spectroscopy. Reznik, M. G.; Chekhovskoi, B. Ya. (Donetsk. Politekh. Inst., Donetsk, USSR). Khim. Tverd. Topl. 1970, (5), 35-9 (Russ). The coal structure was studied using the products of destructive distn., both before and after oxidn. at 20, 90, and 180°. Ir spectra of samples prepd. in liq. petrolatum (1:10) show that oxidn. forms ether bridges and acidic and alc. groups in the coal. Changing the oxidn. temp changes the mechanism of O interaction with the org. matter of coal.

### 1968

3.43 23556r Behavior of germanium during the oxidation of coals. Ryabchenko, S. N. (USSR). Protsessy Term. Prevrashch. Kamennykh Uglei 1968, 370-5 (Russ). Edited by Alekhina, V. I. Izd. "Nauka" Sib. Otd.: Novosibirsk, USSR. Gas and coking coals were oxidized with 30%  $\text{HNO}_3$  for 1 hr. at 90°. The oxidized samples were analyzed for elemental compn., functional groups, and the content of Ge. Oxidn. increased the content of  $\text{H}_2\text{O}$  in the coals, and of its contents of O, OH, CO, and COOH groups. It reduced the contents of C and H. The amt. of Ge solubilized was 48% from gas coal and 15% from coking coal. The oxidized coals were hydrolyzed with 10% KOH; yielding humates. The free humic acids constituted 90% of the combustible part of gas coal; their empirical formula was  $\text{C}_{13.0}\text{H}_{15.1}\text{O}_{3.7}\text{N}_{0.6}\text{S}_{0.1}\text{CO}_{0.03}\text{OH}_{0.2}\text{COOH}_{0.2}$ . The humic acid ash contained Cu, Pb, Zn, Sn, and Ag, as well as smaller



amts. of several other elements. The oxidn. mechanism of gas and coking coals appeared to be different. Oxidn. of gas coal resulted in the introduction of O between the rings yielding humic-like acids, while oxidn. of coking coals was accompanied mainly by the addn. of O on the surface of aromatic systems and was accompanied by splitting of the C-C bonds. A nearly complete degradation of the org. part of gas coal caused the solubilization of 90% Ge. Only 35% Ge was solubilized during degradation of coking coal. This suggests that Ge is present mainly in the form of O-Ge-O bridges.

#### 1966

3.44 104840c Polycondensates obtained from 5-hydroxy-1,4-naphthequinone as model of organic matter of hard coal. Leszek Czuchajowski and Jozef Krzeczek (Wyzsza Szkola Rolnicza, Cracow, Poland). Arch. Gorn. 11(2), 163-74 (1966) (Pol). The ir spectra of 5-hydroxy-1,4-naphthequinone (I) and some of its macromol. derivs. were investigated. Reaction of I with 1,4-benzenebisdiazonium tetrafluoroborate (bisdiazop-phenylenediamine tetrafluoroborate) (II) in H<sub>2</sub>O-acetone gave dijuglonylbenzene. The same reaction performed in 2N Na<sub>2</sub>CO<sub>3</sub> gave a polycondensate with several aromatic units of I or its derivs. joined by phenylene bridges. In the range of 1800-1500 cm.<sup>-1</sup> 2 peaks of quinoid CO origin occurring at 1665 cm.<sup>-1</sup> and 1640 cm.<sup>-1</sup> were less distinct in the polycondensate than in II. Oxidn. of the polycondensate by 2N HNO<sub>3</sub> gave an acid-insol., alkali-sol. fraction with ir spectrum similar to that of humic acids extd. from hard coal, and an acid- and alkali-insol. fraction corresponding to coal humins. 10 references.

#### 1965

3.45 Solubility of coal in tetrahydroquinoline. R. Bruecker and G. Koelling (Bergbau-Forsch. G.m.b.H., Essen, Ger). Grennstoff-Chem. 46(2), 41-3 (1965) (Ger). 1,2,3,4-Tetrahydroquinoline (I) dissolves at 300° 90% of the org. matter of bituminous coal. Part of I forms quinoline with loss of H. Higher-carbon coals are less sol. and require higher extn. temps., which cause side reactions of I. Part of the dissolved matter can be distd. Methylnaphthalenes are obtained at 300°, 4- and 5-ring aromatics at 375°. The soln. mechanism was investigated with model substances and I. Phenyl benzyl ether and dibenzyl ether are split under hydrogenation into PhOH and PhMe, and benzyl alc. and PhMe, resp.

3.46 Infrared spectroscopic characterization of the degree of hydrogenation in the low-temperature hydrogenation of lignite carbonization products. Peter Heinz Berthold and Hans

Koehler. Freiburger Forschungsh. 365A, 37-49 (1965) (Ger). Photographs of ir spectra of lignite carbonization products before and after low-temp. hydrogenation differed, because of the changes in compn. occurring in the hydrogenation, i.e. an increase in the amt. of n-paraffins and the simultaneous almost complete splitting of alkyl-aromatic compds., phenols, and carbonyl compds. Attempts have been made to use these changes of the ir extinction coeffs. of the products before and after low-temp. hydrogenation to characterize the efficiency of the hydrogenation process and to use these changes for process control purposes. The content of aromatic compds. could be estd. by the method of Eckardt, et al. (CA 57, 12790i), so that the percent of aromatically bonded C atoms could be detd. Plotting  $\epsilon_A$  (extinction coeff. of the band at 1610  $\text{cm}^{-1}$  typical for aromatic compds.) against  $\epsilon_{CO}$  (extinction coeff. of the band at 1700  $\text{cm}^{-1}$  typical for carbonyl compds.) always gave a straight line. If, therefore, the extinction coeff. ratio  $\epsilon_A / \epsilon_{CO}$ , found during a control analysis, was on a straight line, characteristic of a particular hydrogenator, the hydrogenation worked effectively. The slope of the line representing the ratio of the extinction coeffs. depends on the age of the hydrogenator and the state of the catalyst employed. If feed material had entered the hydrogenation reactor through a leak in the recuperator, the extinction ratio changed drastically, resulting in a deviation from the straight line previously obtained. Conventional anal. methods for controlling hydrogenator efficiency, e.g. color changes or contents of aromatic compds., were less suitable for control purposes than the ratio of the ir extinction coeffs. for the bands located at 1610 and 1700  $\text{cm}^{-1}$ , resp.

#### 1964

3.47 Hydroxyl groups in coal. B. Roga and M. Weclawska (Abt. Kohlenchem., Katowice, Poland). Brennstoff-Chem. 45(11), 334-6 (1964) (Ger). The vapors of polar liquids such as acetone, methanol, and pyridine cause swelling and crumbling of coal. The simultaneous increase of OH groups, as detd. by the  $\text{Ba(OH)}_2$  or acetylation method, is explained by the splitting of H bonds between OH groups connecting mol. layers. The OH groups may be alc. or phenolic. The  $\text{Ba(OH)}_2$  method is suitable for phenols with  $\text{H}_2\text{O}$ -insol. Ba salts; the acetylation method in pyridine detd. all OH groups unless there is steric hindrance by radicals or rings. Young coals contain more phenolic OH groups, as detd. by  $\text{Ba(OH)}_2$ . In coking coal, OH groups detd. by acetylation are predominant. The OH content as calcd. from the mol. amt. of adsorbed acetone agrees with the results of the  $\text{Ba(OH)}_2$  or acetylation method.

3.48 Hydrogenation of reactive groups in Yallourn brown coal. T. J. Birch and J. D. Blackwood (Div. Chem. Eng., CSIRO, Melbourne). Nature 201 (4921), 797-8 (1964). Coals contg. smalls amts. of O are hydrogenated by direct reaction of H with O. Coals with a high O content show an initial rapid hydrogenation proportional to the O concn., leaving a residual char, which is hydrogenated slowly. The O groups in Yallourn brown coal have a behavior similar to those in lignin. A unit structure is suggested with 5- and 6-membered rings contg. O and attached to  $C_6H_5$  rings. Hydrogenation of this structure would use H and produce  $CH_4$  and  $H_2O$  in the exptl. observed ratio of 2.3:1:0.65, yielding a stable C-ring structure which would condense to form the residual non-reactive char.

3.49 Mechanisms of coal pyrolysis. VI. Reaction patterns in the range 650-850°. Lynne F. Neufeld and N. Berkowitz (Res. Council Alberta, Edmonton, Can.). Fuel (4383), 91-202 (1964), cf. CA 58, 3240b. Detailed measurements of rates of water formation in coal chars at temps. in the range 650-850° are used in conjunction with previously reported data on H yields, wt. losses, and compn. shifts to establish major reaction sequences at >650°. The dominant primary reaction pattern can be completely described by removal of H from lamellar peripheries and pyrolytic deoxygenation, ultimately leading to disengagement of O as  $H_2O$ . Other pyrolytic products evolved from coal chars at >650° e.g.  $CH_4$  and oxides of C, appear to result from secondary C hydrogenation and gasification reactions which are basically unrelated to the thermal decompn. of coal. The relevance of these findings for kinetic studies of coal pyrolysis is discussed.

1963

3.50 Studies on the chemical structure of coal. II. Hydrogenolysis of bituminous coal and humic acids in the presence of the Adkins copper-chromite catalyst. Y. Takegami, S. Kajiyama, and C. Yokokawa. (Kyoto Univ., Japan). Fuel 42, 291-302 (1963); cf. CA 57, 7529b. Hydrogenolysis of Onoura bituminous coal and of humic acids obtained from it by boiling with N  $HNO_3$  was carried out with Adkins Cu-chromite catalyst. The O balances in the hydrogenolysis process and the results of successive oxidn. of hydrogenolysis products indicate that formation of  $C_6H_5$ -sol. products is due to cleavage of O-ether bonds in the coal mol. These products are closely related to the structural unit of the coal mol.

3.51 Infrared spectra of coal: the absorption band at 1600  $cm^{-1}$ . Shuya Fujii (Waseda Univ., Tokyo). Fuel 42 17-23 (1963); cf. CA 57, 14083a. Many causes can be postulated for the very intense absorption band near 1600  $cm^{-1}$ .

in the infrared spectra of coal. The contribution of H-bonded carbonyl groups is discussed. Coals were methylated with  $\text{Me}_2\text{SO}$ , or  $\text{CH}_2\text{N}_2$  or reduced with  $\text{LiAlH}_4$  to eliminate H-bonded carbonyl groups. The infrared spectra and OMe content or the carbonyl content of the original and methylated or reduced coal were compared. For comparison, o-hydroxyacetophenone, which has a H-bonded carbonyl group, was also reduced; the resulting change in the infrared spectra is discussed. H-bonded carbonyl groups in coal are one of the causes for the intense band near  $1600\text{ cm}^{-1}$ , but their contribution to the total absorption intensity at  $1600\text{ cm}^{-1}$  is only about 10-30%. Redn. of coal with  $\text{LiAlH}_4$  is difficult in  $\text{Bu}_2\text{O}$  but takes place fairly readily in dioxane.

1962

3.52 Electrochemical reduction of coal. Heinz W. Sternberg and Irving Wender (U. S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 5943, 10 pp. (1962). The literature on electrochem. treatment of coal is reviewed and possible avenues for further research in this field are discussed. Electrolytic redn. of finely distributed coal results in the addn. of as many as 9 atoms of H to 100 atoms of C. Redn. of coal exts. at controlled potentials indicates the presence of condensed aromatic hydrocarbons and reducible quinones in coal. As much as 65% of low-rank coal can be made alkali-sol. by electrochem. treatment. Higher-rank coals give smaller yields of alkali-sol. products. The nature of this reaction is not clear. The difficulty of reducing coal electrolytically is probably due to the insoly. of the coal and not to any structural peculiarity. Redn. of coal by electrolytically generated radical anions appears to be a promising approach.

3.53 Chemical and physical study of coals in Romania. I. Functional groups with oxygen. Paul Krobl and Iosif Wagner (Univ. "Babes-Bolyai," Cluj, Romania). Studia Univ. Babes Bolyai, Ser. Chem. 8(1), 478-86 (1968). The functional groups ( $\text{COOH}$ , acid and nonacid OH, and CO) of 5 indigeneous coals of different degrees of metamorphosis were studied. The coals examd. were: lustrous brown coal Codlea (Lower Jurassic, Liasic), brown coal Petrila (Lower Neogene, Aquitanian), bituminous coal Lupeni (Lower Neogene, Aquitanian), gas coal Lupeni (Lower Neogene, Aquitanian), and fat coal Secul (Upper Carboniferous, Stephanian). The coal samples were kept under water, finely ground, dried in an inert gas atm. ( $\text{CH}_4$ ) at  $100-110^\circ$ , and finally screened. The results showed that the  $\text{COOH}$  and phenolic OH were most sensitive to changes induced by metamorphosis, since these groups disappeared almost completely in coals with the most advanced degree of metamorphosis.

The CO group showed a higher resistance to geochem. factors. The % nonreactive O also decreased with increasing degree of metamorphosis, but the ratio of nonreactive O to total O increased with the degree of metamorphosis. This was interpreted by assuming that, with increasing coal metamorphosis, the O entered into aromatic rings, forming heterocyclic bonds, and that simultaneously the ultrafine capillarity of the coal was destroyed gradually, so that accessibility to the reagents was diminished. By assigning hypothetical formulas to the 5 coal mols. ( $C_{60}H_{15}O_3$ ,  $C_{60}H_{40}O_6$ ,  $C_{52}H_{45}O_5$ ,  $C_{50}H_{42}O_4$ , and  $C_{50}H_{41}O_3$ ) and comparing them with the % at. COOH content, the 5 mols. contained 1, 0.5, 0.34, 0.25, and 0.12 COOH groups, resp., thus confirming the increasing aromaticity of the coals with increasing metamorphosis and the increasing size of these mol. units, since fractions of functional groups cannot exist. 17 references.

3.54 The assignment of the  $1600\text{ cm}^{-1}$  band in the infrared spectrum of coal. H. S. Rao, P. L. Gupta, Mrs. F. Kaiser, and A. Lahiri (Central Fuel Res. Inst., Jealgora, Bihar India). Fuel 41, 417-23(1962). The infrared absorption spectra of Jambad-Bowlah coal and its HCONMe<sub>2</sub> ext. were examd. in the range of 5000 to  $670\text{ cm}^{-1}$ . Both the coal and the ext. were reduced by treatment with LiAlH<sub>4</sub> in ether soln. Comparison of the spectra of the reduced materials, as well as the residual products on carbonizing the coal and the original ext. to  $490^\circ$ , does not favor the assignment of the intense  $1600\text{ cm}^{-1}$  band principally to carbonyl. An interpretation of the vibrational spectrum has been made on the basis of a polynuclear condensed aromatic nucleus, the aliphatic moiety being made up principally of CH<sub>2</sub> rings. The evidence indicates the presence of 2 types of OH groups, one more strongly H bonded than the other. The spectra also suggest the presence of small amts. of CO located in structural environments that cause frequency-lowering effects. The spectroscopic data do not favor the hypothesis of completely satd. structures involving many tetrahedral C-C bonds over the polynuclear condensed aromatic structure concept.

3.55 Oxygen groups in Donets Basin coals. Samir Sarkar (Indian Inst. Technol., Bombay). Fuel 41, 206-8 (1962). The Donets Basin in the U.S.S.R. contains bituminous coals of rank varying from that of a long-flame coal to that of a semi-anthracite and even an anthracite. Samples of these coals were analyzed for O-contg. functional groups. CO<sub>2</sub>H groups were detd. by ion-exchange by using Ba(OAc)<sub>2</sub>. OH groups were detd. by acetylation with Ac<sub>2</sub>O and anhyd. NaOAc. CO groups were detd. by reaction with phenylhydrazine. Results for 5 coals are presented together with their ultimate analyses and volatile-matter contents. The content of O-contg.

functional groups decreases with increase in coal rank. Carbonyl O falls with increase in rank of coal, but 0.1% is present even in coals contg. 90% C. Hydroxy O falls rather sharply from 6.8% to 1.3%, but then slowly decreases to 0.6% for the lean caking coal. Graphs are given for the variation of the ratio of OH O to total O with changes in C content of the coal.

3.56 Ring analysis and spectral characterization of resins from pitch of low-temperature tar. C. Karr, Jr., J. R. Comberiat, and Patricia A. Estep (Bur. of Mines, Morgantown, W. Va.). Fuel 41, 167-76 (1962). The resins from the pitch of lignite and subbituminous and bituminous low-temp. tars were characterized by ring analysis, infrared spectra, and ultraviolet spectra. The resins were found to be basically aromatic compds., all having 4 or 5 aromatic rings per mol., these being mostly isolated single aromatic rings and some clusters of 2 fused aromatic rings. Satd. rings, possibly including ether groups, are also fused into the hydrocarbon skeleton. The lower-mol.-wt. resins apparently have a linear arrangement of rings with 1 or 2 satd. rings in addn. to the aromatic rings. The higher-mol.-wt. resins apparently have a globular or compact arrangement of rings with 5-7 satd. rings in addn. to the aromatic rings. The resins have 2-6 O atoms per mol. Phenolic OH groups are present and probably account for most of the O. CO groups are also present, they are conjugated with either aromatic rings or olefinic groups or both. The OH and CO groups are not on adjacent C atoms and the CO group is probably not quinoid. Most aromatic rings have at least 2 substituents, these are mostly either Me groups, fused satd. rings, or both. Alkyl substitution is greater for the lower-mol.-wt. resins.

#### 1961

3.57 Chemical and petrographic character of the products of hydrogenation of fusainized microcomponents. D. T. Zabrannyi and S. Nasritdinov. Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Met. i Toplivo 1961, No. 5, 144-9. The hydrogenation of fusainized microcomponents (I) was studied on a hand-picked sample of Angren brown coal contg. fusain 62, semifusain 8, xylite 8, and vitrain 2%. The hydrogenation was carried out in a rotating autoclave, heated elec. at 360, 380, 400, 425, and 450° for 8 hrs. Redn. depolymerization, occurring during hydrogenation of I, causes the transformation of fusain to semifusain and then to xylite. With further depolymerization, the I lose their cellular structure and become amorphous. Simultaneously their reflectivity becomes identical to that of vitrainized substance. This process is accompanied by the formation of sol. hydrogenated material and, to

a certain degree, by condensation and formation of products having an increased reflectivity. The xylite structure is not restored during condensation. With increased degree of hydrogenation of I, the chem. properties of the insol. hydrogenated material become similar to those of the coal and, after hydrogenation at 450, become identical to those of lean coals with respect to volatile matter and elemental compn. Fusains of brown coals hydrogenate easily because they contain a large amt. of nonreactive O, 70% of which is hydrolyzable. Fusains of higher-rank coal hydrolyze with difficulty or not at all because they contain little O, this O is chiefly in carbonyl groups.

#### 1960

3.58 Ether oxygen in coal. J. N. Bhaumik, A. K. Mukherjee, P. N. Mukherjee, and A. Lahiri (Central Fuel Res. Inst., Dhanbad, India). Am. Chem. Soc., Div. Gas Fuel Chem., Preprints Sept. 1960, Vol. 1, 113-116. Ether O present in coals of different rank has been est. by HI treatment. The major fraction of unreactive O in coal is present in ether combination. Low-rank coals are characterized by the presence of mixed ethers.

#### 1959

3.59 Chemical constitution of coal. C. Yokokawa, S. Kajiyama, Y. Watanabe, and Y. Takegami (Univ. Kyoto, Japan). Proc. Symp. Nature Coal, Jealgora, India 1959, 194-202. The N HNO<sub>3</sub> oxidn. of 30 model substances shows that selective oxidn. occurs at H-rich positions in coal. The properties of 12 derivs. of humic acids regenerated from bituminous coals are described. The humic acid unit is considered to have a mol. wt. of 600 and one ether linkage, corresponding to a condensed aromatic structure of 3 or 4 rings.

3.60 Brief examination of the relation between internal surface and functional group measurements of coals. I. G. C. Dryden. Proc. Symp. Nature Coal, Jealgora, India 1959, 112-18. The surface area of coal was crit. examd., and the possible influence of functional groups on this area was evaluated. Bituminous coals have sp. internal surfaces in the range of 30-100 sq. m./g., situated almost entirely in the ultrafine capillaries of widths <40 Å, and accessible only through constrictions of widths 5-8 Å. The heat evolved on wetting a unit surface increases by a factor of up to 4, and adsorption per unit of surface in equiv. conditions also increases along with the content of accessible O-contg. groups if the liquid or

vapor mols. are polar. Chem. methods for estg. reactive O groups are chiefly detd. by the chem. nature of the reagent and the reaction conditions employed; here, mol. sieve effects are of secondary importance. Of the O in bituminous coals, 70-90% occurs as OH and quinone groups, the former probably exceeding the latter except in coking- and higher-rank coals. Phys. methods for estg. O groups are unsatisfactory.