4. Bridged Ring Cracking

1970

4.1 144340m Analysis of the chemical structure of coal by investigations on the high-pressure hydrogenolysis reaction mechanism. I. Hydrogenolysis and hydrogen distribution of the reaction products. Maekawa, Yousuke; Ueda, Sigeru; Hasegawa, Yoshihisa; Yokoyama, Shinichi; Hiroki; Eizo; Yoshida, Yuji (Gov. Ind. Dev. Lab. Hokkaido, Japan). Nenryo Kyokai-shi 1970, 49 (524), 908-16 (Japan). Coal contg. moisture 1.1, ash 6.8, volatile matter 43.6, and fixed C 48.5% was hydrogenolyzed for 26-206 min at 400° and 100 kg/cm^2 initial H pressure. The hydrogenolysis was considered as a rate process, and the consecutive reaction was expressed as going from the pyridine ext. at room temp. to the C_6H_6 Soxhlet ext., followed by the n-hexane Soxhlet ext. and the n-hexane ext. at room temp. The main reaction occurring during the hydrogenolysis was the destruction of bridges (except for α-CH_2 groups) between structure units. The aromatic end rings could become slightly satd. in going from the pyridine ext. to the benzene Soxhlet ext.

1969

4.2 6352y Depolymerization of high-sulfur coal of the Novometelkinsk deposit. Baranskii, A. D.; Rodionova, L. E. (USSR). Izv. Nauch.-Issled. Inst. Nefte-Uglekhim. Sin. Irkutsk. Univ. 1969, 11(Pt. 1), 79-80 (Russ). In an anal. of org. S, the coal was catalytically depolymd. for 2-24 hr at 176 and 185° in the presence of p-toluenesulfonic acid in phenol. The depolymn. occurs on the methylene bridges and phenol combines with the depolymd. coal. By measuring the phenol consumed, an av. mol. wt. of 260-70 is found. The main depolymn. process criteria is the yield of the MeOH-benzene-sol. fraction. During the depolymn. some H_2S was detected, owing to breaking of the S bonds in thio ether or bis thio ether groups.

1968

4.3 62881n Mechanism of the hydrogenation of coals and petrographic components. Nasritdinov, S. (USSR). Ugli Srednei Azii Puti Ikh Ispol's. 1968, 151-8 (Russ). Edited by Starobinets, I. S. Izd. "Fan" Uzb. SSR: Tashkent, USSR. The temps. at which the connecting links between the structural units of coals are destroyed, the probable order of hydrogenation of the units, and the products formed and their soly. in benzene, petroleum ether, and pyridine are discussed.

1967

4.4 51871w Measurement of the ratio of aromatic hydrogen to aliphatic hydrogen by infrared spectrometry, and the relation between nonaromatic hydrogen and the softening tempperature of coals. W. Fassotte and M. Saussez. Ann. Mines Belg. 1967 (7-8), 779-93 (Fr-Neth). The following equation shows the relation between the ratio of the aliphatic + alicyclic (H_{al}) to the aromatic H content (H_{ar}) of polycyclic hydrocarbons and the integrated amt. of energy absorbed in the in the 3020-200 cm.$^{-1}$ region of the ir spectrum. $H_{al}/H_{ar} = 0.30\ F_{al}/F_{ar}$, F_{al} and F_{ar} are the planimetric surfaces corresponding to the aliphatic CH and aromatic CH bonds located in the 2800-3050 and the 3020-200 cm.$^{-1}$ band, resp. The softening temp. of coal increases with H_{al} because low-temp. pyrolysis induces cleavage of polycyclic hydrocarbons at methylene bridges. On the other hand, the softening temp. of coal increases with its hydroxylic H concn. (H_{OH}) because the departure of a phenolic group at low pyrolysis temp. favors polymn. by establishing a biphenyl bridge between two polycyclic mols. To take account of this effect of H_{OH} on the softening temp., the ratio H_{al}/H_{ar} of the above equation must be replaced by the following value. $H_{al}/(H_{ar} + H_{al}) \times (H_t - H_{OH})/H_t$, in which H_t is the wt. % of total H in the coal sample. The value of H_{OH} is calcd. from the wt. % hydroxyl O (O_{OH}) of the sample detd. from the total O content, O_t, by using the equation $O_{OH} = -2.07 + 0.89\ O_t$.

4.5 53442b Mechanism of hydrogenolysis of coal under high pressure. Maekawa, Yousuke, Shimokawa, Katsuyoshi, Ishii, Tadao, Takeya, Gen (Gov. Ind. Develop. Lab., Japan). Nenryo Kyokaishi 1967, 46 (488), 927-34 (Japan). Yubari coal was hydrogenated under 220-30 kg./cm.^{2} H pressure at 400 and 450° with "red mud" as catalyst. The nominal reaction time was changed from 0 to 120 min. No oil vehicle was used. The reaction product was fractionated by a n-hexane and benzene into 5 fractions and the yield of each fraction was detd. The structural parameters of each fraction of the hydrogenated products were calcd. from the contents of the different types of H measured by high resolution N.M.R. spectroscopy (60 Mc.) and from the elemental compn. of each fraction. From the change of yield of these fractions, the change of resp. structural parameters of the mean structural unit, and the change in mean mol. wt. measured by vapor pressure osmometer, the mechanism of the hydrogenolysis of coal under these exptl. conditions was surmised to be as follows. While part of the coal was converted directly into oil-1 (including gas and water), the main process of coal hydrogenolysis can be described by the following reaction scheme. coal → asphaltene → oil-2 → oil-1 (including gas and water). The main chem.

reactions occurring during coal hydrogenolysis were assumed to be: at 400°, destruction of bridges between unit structures and dealkylation in the unit; at 450°, destruction of bridges between unit structures, dealkylation in the unit, and hydrocracking of the aromatic ring. The mean structural unit of asphaltene obtained from Yubari coal hydrogenated products appeared to be 3 or 4 condensed aromatic rings, and it showed a form ranging from dimer to tetramer.

1966

4.6 The structure of coals of different rank; hydrogen distribution of depolymerization products. Laszlo A. Heredy, Andrew E. Kostyo, and Martin B. Neuworth (Res. Div., Consolidation Coal Co., Library, Pa.). Advan. Chem. Ser. No. 55, 493-500, discussion 501-2 (1966) (Eng). The distribution of H types in the sol. fractions from the depolymerization of a series of coals was detd. by N.M.R. analysis. The aromatic H content varied from 20 to 32% of the total H, and no simple relation existed with coal rank. β-Paraffinic and naphthenic H, the major types, exceed the α-H, and comprise 38-66% of the nonaromatic H. The most striking variation in the structure of the 6 coals was the no. of methylene bridges. The degree of depolymerization could be correlated directly with the no. of methylene bridges found in the sol. fractions. A general coal structure, in accord with the results, consists of large units((mol. wt. $>$ 4000) and smaller units (mol. wt. 300-600) connected by methylene bridges.

4.7 Acids obtained by oxidation of Central Asia coal with oxygen under pressure. Z. I. Povzner, Z. A. Rumyantseva, N. M. Karavaev, B. B. Gartsman, and I. I. Rakitin. Dokl. Akad. Nauk Tadzh. SSR 9(2), 24-8 (1966) (Russ). Study was made of the acids obtained from 8 samples of coal and 4 samples of brown coal. Oxidn. was performed in an autoclave with 6 g. coal, 24g. NaOH, 126 g. H_2O, C:O ratio 1.90:1 1 hr. at 260-70°. The presence of CO_2, oxalic acid, volatile acids, and aromatic and insol. acids was detd. Dibasic and polyfunctional acids, a small amt. of BzOH, and high-mol.-wt. acids with polynuclear structure were also detected. Tables of chem. compns. of different fractions are presented.

4.8 Swelling equilibrium of coal by pyridine at 25°. Y Sanada and H. Honda. (Resources Res. Inst., Kawaguchi, Japan) Fuel 45(4), 295-300 (1966) (Eng). The mol. wt. per cross-linked unit, M_c, of coal was estd. by applying the equation of Flory-Rehner (CA 38, 291^6). The value of M_c over the range 65-80% C content is almost constant. For caking coal and coking coal, M_c increases suddenly with rank to a max. at about 85% C for Japanese coals, then decreases with rank increase. This relation agrees well with that between max.

fluidity, measured by Gieseler plastometer and rank of coal. The degree of cross-linking may be an important factor in detg. the mech. and thermal properties of coal. 9 references.

4.9 Chemical constitution of coal. XI. Examination of subhumic acids produced by ozonization of humic acid. G. J. Lawson and J. W. Purdie (Univ. Birmingham, Engl.). Fuel 45(2), 115-30 (1966) (Eng); cf. CA 50, 17378f; 53, 5635d; 62, 11583g. Humic acid was ozonized in an aq. medium, and the ether-sol. products were resolved by ion-exchange chromatography. Glycolic, mesoxalic, succinic, (±)-malic, mesotartaric, (±)-tartaric, 2-oxoglutaric, oxamic, and nitrolotriacetic acids, and oxallyglycine were identified in the resulting fractions and also oxalic, glyoxylic, benzenepentacarboxylic and mellitic acids. The 1st group of products represented mainly the aliphatic part of the humic acid mol. and the 2nd group the aromatic part. The humic acid, and hence the parent coal, probably consisted of small aromatic units linked by short, mainly unbranched, aliphatic chains contg. some of the N as tertiary and perhaps secondary amines. Single CH_2 bridges appeared to be particularly significant in the humic acid structure. 25 references.

1964

4.10 Chemical identification of methylene bridges in bituminous coals. L. A. Heredy, A. E. Kostyo, and M. B. Neuworth (Consolidation Coal Co., Library, Pa.). Fuel 43(5), 414-16 (1964) (Eng). Diarylmethanes are possible repeating units in bituminous coals; depolymerization of coal with phenol-BF_3 was suggested as a test for structures of this general type. Complete aromatic interchange of a diarylmethane with phenol can produce dihydroxydiphenylmethane, which is dehydroxylated by the Kenner and Williams procedure (CA 49, 6865b) to diphenylmethane. These methods were applied to the C_6H_6-sol. ext. from the depolymerization of Ireland Mine coal and the identity of the diphenylamine was established by its ir spectrum. Since ^{14}C-labeled PhOH was used in the aromatic interchange step, ^{14}C was found in the products, the analysis was in agreement with a structure contg. 2 labeled benzene rings and a labeled CH_2 bridge. The yield of diphenylmethane corresponded to 2% of the total H in the coal present as CH_2 bridges compared with 5.4% from N.M.R. analysis. This difference may be partly due to the limited selectivity of the dehydroxylation reaction; also, N.M.R. analysis measures all the CH_2 bridges including diarylmethanes other than dihydroxydiphenylmethane.

4.11 4790p Preparation of regenerated humic acids by the oxidation of coals with air. I. Oxidation of coals with air. Vicente Gomez Aranda, Fermin Gomez Beltran, and Clemente Romero Linan (Inst. Nacl. Combustible, Consejo Super. Invests. Cients., Saragossa, Spain). Combustibles (Zaragoza) 23, 29-63 (1964) (Span); cf. following abstr. For the prepn. of regenerated humic acids, coal was gasified with air or O and heated to 150-300° either in a stationary phase or in a fluidized bed and varied between 200 and 400 hrs. to yield 80-90% humic acid. The operating conditions and yields depended on the degree of coalification of the initial material and its ash content. The oxidized coal was treated with KOH or NaOH soln., acidified, and the pptd. humic acids were filtered and dried in a vacuum oven. With long aeration times, the humic acid yield decreased with an increase in temp. With short aeration times, the yields increased or decreased, depending on the individual coal. This phenomenon was explained by the fixation of O, mainly through formation of CO_2H and OH groups, as well as by the release of CO_2 through oxidn. of CH_2 groups of the side chains and methylene bridges. The humic acids were studied and results were evaluated as a function of time. From CZ 1966 (35), Abstr. No. 2802.

1962

4.12 Low-temperature depolymerization of bituminous coal. L. A. Heredy and M. B. Neuworth (Consolidation Coal Co., Library, Pa.). Fuel 41, 221-31 (1962). A high-volatile bituminous coal was treated with $PhOH-BF_3$ at 100°. Extensive depolymerization occurred as measured by soly. in PhOH (I). Over 60% of the treated coal was sol. in I, as compared with 19.9% in a blank expt. on coal with I alone. The degradation of the coal is interpreted as an "aromatic interchange" reaction involving cleavage of aliphatic-aromatic linkages and exchange of the aromatic structures with I. The chemistry of this aromatic interchange was demonstrated by reaction of I with model compds. consisting of substituted phenols connected to naphthalene by methylene and ethylene linkages. One or both of the aromatic structures in the model compds. exchanged with I.