2. Catalytic Effects of Ash

1973

2.1 Catalysis of Coal Gasification at Elevated Pressures. W. P. Haynes, S. J. Gasior and A. J. Forney (Bur. Mines) 165th ACS Natl. Meet. (Dallas 4/8-12/73) ACS Div. Fuel Chem. Prepr. 18 #2:1-28 (1973). Screening tests on 10 g samples of a high-volatile bituminous coal plus 0.5 g of catalyst, conducted by the U. S. Bureau of Mines, were made at 850°C, 300 psig, and 5.8 g/hr of steam carried by 2000 cu cm/hr of nitrogen. All of the 35 additives tested, including Raney nickel, and iron, bismuth, boron, lead, copper, and zinc oxides, increased the total gasification rate and the yields of desirable gases (methane, hydrogen, carbon monoxide). The effects of temperature, steam rate, gasification time, and method of catalyst admixture were investigated. Potassium salts in ash residues from total coal gasification still retained most of the activity for producing methane, lost part of ability to increase hydrogen production, but inhibited carbon monoxide production. Pilot-plant trials adding lime or dolomite at 5% concentration to coal fed to a 4 in. dia Synthane gasifier system resulted in significant increases in yields of methane, hydrogen, and carbon monoxide. Tables.

1971

2.2 65947g Effect of inorganic impurities and additives on caking ability of coals. Iskhakov, Kh. A.; Prilepskaya, L. L.; Ovechkina, L. E. (Kuzbasskii Politekh. Inst., USSR). Khim. Tverd. Topl. 1971, (3), 122-5 (Russ). Ash accumulated in the fine classes of the high-volatile Kuznetsk and Karaganda coals, decreased their cokability. The effect of the ash components, like that of the exptl. introduced quartz sand, kaolin, CaO, and FeO, increased with their increasing sorption capacity in respect to the thermobitumens, e.g. the effect of FeO and CaO was greater than that of SiO_2. The deteriorating effect of the ash components was eliminated by screening off the 3-0 mm coal fraction and intensive mixing of the coal charges in order to attain uniform distribution of the poorly sintering coal classes.

1970

2.3 113758g Hydrocracking process using a coal-derived ash. Gatsis, John G. (Universal Oil Products Co.) U.S. 3,707,461 (Cl. 208-111; C 10g), 26 Dec 1972, Appl. 99,677, 18 Dec 1970; 3 pp. Coal ash may be used as the catalyst in hydrocracking heavy hydrocarbons, particularly those from solvent extn. of coal. Thus, the residue from solvent extn. of coal is sepd., coked at $\leq$1150°F, and burned to complete combustion in air at the same temp. A 25:75 mixt. of ash and the combined products of solvent extn. and coking is charged to a hydrocracking zone at $\sim$900°F. H at $\leq$135 atm is passed through the mixt. at $\sim$10,000 ft^3/hr-bbl of oil. The catalyst and the undissolved coal are spd., coked, and burned to produce more catalyst.

2.4 77654p Coal liquefaction process using ash as a catalyst. Gatsis, John G. (Universal Oil Products Co.) U.S. 3,671,418 (Cl. 208/10; C 10g), 20 Jun 1972, Appl. 99,676, 18 Dec 1970; 4 pp. Solid carbonaceous material is mixed with a suitable hydrocarbon solvent and catalytically active ash, the latter being an ash from the decarbonization of coal, and subjected to solvent-extn. conditions in the presence of H, and sepn. of the liq.-hydrocarbon residue from the resultant mixt. Sepn. of the catalyst from the undissolved coal in order to reuse it is no longer necessary. Catalysts can be produced by the process itself, and the poisoning and coking that inactivate other catalysts do not take place. The liq. residuum sepd. from the solid residuum in the effluent from the solvent-extn. zone is further processed by distn. and fractionation and solvent is recovered and recycled to provide a continuous supply of solvent for the extn. process. The solid residuum is subjected to coking conditions at $<$1150°F. to produce the catalytic ash and recover the volatile content.

1969

2.5 127068z Effects of minerals on the caking ability of coal. Gaberman, B. G.; Khalitov, I. Z. (USSR). Tr. Khim.-Met. Inst., Akad, Nauk Kaz. SSR 1969, 5, 8-14 (Russ). The effects of 3.5-10% albite, orthoclase, pyrite, siderite, clinochlore, chalcedony, quartz, biotite, and calcite on the caking of coal were detd. All except the 1st 3 increased the swelling of the coal when 3.5% mineral was added; when 10% was added, only siderite did. Plastometer curves were obtained for mixts. of coal with quartz, kaolin, gypsum, and the minerals mentioned. Because of its surface properties, kaolin had the max. effect on the shape of the plastometer curve.

2.6 52016v Interaction of a plastic coal mass with some mineral substances. Kutovoi, P. M.; Bruk, A. S.; Goncharov, V. F.; Bezbakh, Zh. I. (Dnepropetrovsk. Met. Inst. Dnepropetrovsk, USSR). Khim. Tverd. Topl. 1969, (3), 13-17 (Russ). The effects of adding up to 60% SiO$_2$, CaO, FeO, or an iron ore magnetic concentrate on the properties of a plastic coal depend on the thermophys. and adsorption properties of the additive. Increasing its amt. leads to an increased temp of formation of a mobile liq. phase, a decrease in the temp. interval of min. viscosity, and changes in the max. viscosity.

2.7 Coal hydrogenation. Ronald H. Wolk, Edwin S. Johanson, Seymour B. Alpert (Hydrocarbon Research, Inc., NY), U. S. 3,617,465 (Cl. 208/8; C 10g) 20 Nov 1969, Appl. 878,268. A coal hydrogenation process employing an expanded particulate solids bed wherein the solids are derived from the coal which is placed in random motion by the upflow of a slurry of coal, hydrocarbon liquid and hydrogen to produce better than 80 per cent conversion of coal to gas and liquid synthetic petroleum products. The particulate solids bed is derived from the coal being fed to the reaction zone.

1968

2.8 Use of spherical catalyst in coal extract hydrogenation. Frank B. Sprow, Grady W. Harris (Esso Research and Engineering Co.), U. S. 3,575,847 (Cl. 208/112; C 10g) 5 Dec 1968, Appl. 781,475. Coal extracts containing suspended solids are hydrotreated in a fixed-bed downflow reactor. Bed plugging is minimized by using substantially spherical catalyst granules having a minimum diameter at least ten times as great as the maximum dimensions of the suspended solids and maintaining a flow rate above the minimum at which occlusion of the bed results, preferably at least 1000 pounds per hour per square foot.

2.9 14807h Change in the weight and ash content of coals during oxidation. Nazarova, N. I.; Mozhaeva, V. I.; Alybakova, N. (USSR). Sb. Statei Aspir. Kirg. Gos. Univ. 1968 No. 2, 130-40 (Russ). The wt. increase G, in the oxidn. of dry brown coal and of long-flame coal, was 2.9 and 0.7%, resp., in 170 days at room temp. Oxidn. for a year changed G to 0.84 and 1.65%, respec. Under leaching conditions the wash H_2O contained Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, SO_4^{2-}, and Cl^-. The dried residues contained sesquioxides and SiO_2.

2.10 144335p Decomposition of coal substances of Northern Bohemian lignites under increased pressure. Konrad, B. (Czech.). Tuha Paliva 1968, 1(2-3), 92-6 (Czech). Increasing the pressure during lignite gasification (1-100 kg/cm^2, 500-600°) increased the semicoke yield and decreased the tar yield. Gas obtained at high pressure contained more CH_4 and less H. Increasing the content of ash in lignite increased the yield of semicoke and gas, which had a high CO_2 content and a low hydrocarbon concn. Increasing the gasification temp. decreased the semicoke and tar yield and increased the gas yield.

1967

2.11 30656f Characteristics of coals of the same coal seam as a function of ash content. Hino, Yoshinori (Mitsui Mining Co., Japan). Nenryo Kyokai-shi 1967, 46(483), 539-54 (Japan). Regression equations for coals of the same source, showing the relation between ash content and other characteristics, e.g., moisture, volatile matter, fixed C, calorific value, ash compn., and fixed S, are given. These equations show values of significant levels within 1% of the detd. values with only a few exceptions. The equations are derived and examd. by use of anal. data on coals from the same sources in Japan.

2.12 66399b Caking properties of highly concentrated Kuznetak coals. V. S. Kaminskii. Kohs Khim. 1967 (5), 7-11 (Russ). A study of the changes occurring in the ash content and petrographic compn. on benefication of Kuznetsk coals showed that the increase in the caking properties, as measured by the thickness of the plastic layer, of highly concd. fractions was not directly related to the decrease in their ash contents. There was also no direct relation between the total amt. of gelified vitrinite mass or amorphous vitrinite contained in the coal conc. and its improved caking properties. An important factor contributing to the improvement of the coal conc. could be the liberation into it of very light fractions of vitrinite having good caking properties. 17 references.

1966

2.13 The effect of inorganic contaminants in the TTH (Low Temperature Hydrogenation) process. G. Guenther (VEB Hydrierwerk Zeitz) Chem. Tech. (Berlin) 18 #6:358-62 (June 1966). Lignite ash or salts of various inorganic elements found in the ash were incorporated into the 25% tungsten disulfide/5% nickel sulfide/activated alumina catalyst commonly used in low-temperature hydrogenation of lignite tar oil to petroleum-like products in order to evaluate the extent to which ash constituents are responsible for the rapid activity loss of this catalyst in service. The effects of the harmful elements were pronounced only after high-temperature treatment of the catalyst in the oxidic state corresponding to the conditions of oxidative regeneration. The most harmful elements proved to be sodium (as the carbonate or hydroxide), arsenic, phosphorus, iron, and surprisingly, nickel, which is a necessary component of the catalyst. The effects of added graphite, alumina, calcium sulfate, zinc sulfate, and tungsten trioxide were so slight as to be attributable to a dilution effect. Aluminum sulfate had a slight promoting effect, which was probably due to structural changes in the catalyst. Tables. (in German)

2.14 20881d Effect of oxidation on composition and properties of mineral fraction of some coals from Kuznetsk Basin. M. S. Sharlovskaya, N. A. Sinaiskii, and A. G. Merkulov (Inst. Phys.-Chem. Principles of Mineral Raw Maters. Process., Novosibirsk). Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Tekh. Nauk 1966(2), 139-47 (Russ). Three kinds of Kuznetsk coals were investigated. While increasing coal oxidn., the content of CaO in coal ash increases with decrease in content of SiO_2, Al_2O_3, and water-sol.-compds. of Ca, Mg, and S, resp. The sintering expts. and the x-ray analysis (Sinaiskii, et al., CA 62, 7544f) were used in detg. the trend to form solid ash deposits. Ash briquets from all of the oxidized coals exhibited a strength min. at 800° and a max. at 900-1000°, presumably because of formation of alumocalcium silicates and free CaO, resp. In com. fuel combustion the trend to sintering of fly ash changes in a different way; the formation of anhydrite (due to sulfation of free CaO) takes place in the presence of SO_3 in the top gases and the ash sinters at every temp. $< 850°$. Effect of the presence of different mineral compds. on the temp. characteristics of ash is discussed. 11 references.

2.15 57673p Thermographic analysis in studying the pyrolysis of peat ash and semicoke. V. E. Rakovskii, M. V. Engel'ne, and M. V. Popov (Polytech. Inst., Kalininsk). Izv. Vyssh. Uchcb. Zaved., Khim. Khim. Teknol. 9(4), 654-8 (1966) (Russ). Peat samples, ashed at 300-800°, were subjected to differential thermal analysis (heating rate: 10°/min. to 800° in the absence of air). Marked changes in the mineral portion were noted and chem. interactions of the minerals with liberation of heat in the range 500-600°. An endothermic effect observed at 660-690° increased with the increasing temp. of ashing; and reached a max. when the ashing temp. was 600°. The thermal effect accompanying high-temp. destruction was assigned principally to interaction with org. substances of aromatic nature.

1965

2.16 79261z Composition and properties of ash of oxidized Kuznetsk Basin coals. Sharlovskaya, M. S.; Sinaiskii, N. A.; Merkulov, A. G. (USSR). Gorenie Tverd. Topl., Tr. Vses. Konf., 2nd 1965 (Pub. 1969), 499-508 (Russ). Edited by Yavorskii, I. A. Izd. "Nauka" Sib. Otdel.: Novosibirsk, USSR. Mineral ash of 3 types of oxidized Kuznetsk basin coals from open-cut mines contained considerable amts. of CaO in the form of calcite. Calcination expts. and x-ray anal. of the ash showed that the max. calcination tendency in an oxidizing medium during sintering at 900-1000°C was accompanied by the formation of binding Al Ca silicates and of free CaO. Under industrial conditions in the presence of SO_3 in smoke gases, calcination of this ash took place at $<850°$ due to sulfation of free CaO. The ash of oxidized coals interacted strongly with H_2O, causing rapid hardening of the ash.

2.17 The removal of metallic contaminants from coal extracts. Everett Gorin (to Consolidation Coal Co.). U. S. 3,184,401 (Cl. 208-8), May 18, 1965, Appl. Jan. 19, 1962; 3 pp. The ext. from the solvent extn. of coal contains metallic contaminants which interfere with further processing. These contaminants are removed by acid in the presence of an H-transferring hydrocarbonaceous liquid, such as a di-, tetra-, or octahydro deriv. of anthracene or phenanthrene. The liquid prevents degradation of the ext. For example, coal is extd. by using a solvent from a previous hydrogenation run. About 90% of the solvent is then recovered by distn., the remaining 10% in the ext. supplying the above-mentioned liquid. The ext. is then deashed with aq. HCl at 315° and 1600 psig. at an ext./acid ratio of 1.0. The deashed ext. is then hydrogenated. Because of the deashing, 620 lb. of ext./lb. catalyst can be hydrogenated as compared with only 75 lb. of ext. if the ext. was not deashed. Cf. U. S. CA 56, 13176g; CA 61, 10510b.

1962

2.18 Method of attriting solids in a hydrocracking process. William B. Retallick (Consolidation Coal Co.), U.S. 3,275,546 (Cl. 208-108), 28 Dec 1962, Appl. No. 247,963. The process for catalytically hydrocracking ash-containing coal extract which comprises: (a) establishing and maintaining a bed of catalyst in a catalytic hydrocracking zone, (b) introducing ash-containing coal extract in a liquid state into the hydrocracking zone, (c) maintaining the flow of liquid through the bed of catalyst under hydrocracking conditions at a velocity between 0.01 and 1 ft./sec. to maintain the catalyst as a liquid-phase, dense fluidized bed, whereby a portion of the ash-containing extract is converted to distillate products and at least a portion of the ash in the extract is deposited upon the catalyst, and (d) recycling at least a portion of the unconverted coal extract in the liquid state into a local region of the liquid-phase, dense fluidized bed at a velocity between 5 and 50 feet per second, whereby a zone of relatively high turbulence is created in a portion of the bed wherein the ash-laden catalyst is attrited and thereby reactivated.

2.19 Process for producing hydrogen-enriched hydrocarbonaceous products from coal. Everett Gorin, Robert T. Struck, and Clyde W. Zielke (Consolidation Coal Co.), U. S. 3,232,861 (Cl. 208-8), 22 Aug 1962, Appl. No. 218,769. An improved process for producing hydrogen-enriched hydrocarbonaceous products from coal, which process comprises (a) subjecting said coal to solvent extraction to yield ash-containing extract, said ash comprising alkaline ash components and inert ash components, (b) treating at least a portion of said ash-containing extract in a deashing zone to preferentially remove alkaline ash from said ash-containing extract so as to yield a deashed extract containing a lower proportion of alkaline ash to inert ash than said ash-containing extract, (c) subjecting at least a portion of said deashed extract to hydrogenation in a hydrogenation zone in the presence of a catalyst to yield hydrogen-enriched hydrocarbonaceous products, whereby said ash components contained in said deashed extract deposit on the catalyst particles thereby causing said catalyst particles to lose activity, and (d) subjecting at least a portion of the ash-containing catalyst particles to an abrasion treatment to selectively remove a uniform thin outer layer therefrom such that the resulting abraded catalyst has an increased catalytic activity.

1961

2.20 Desulfurization of coals at low temperatures by gaseous desulfurizing agents. I. Attempts to desulfurize certain coals from the Yiu valley by oxidation in a fixed bed. I Blum and V. Cindea. Acad. Rep. Populare Romine, Inst. Energet., Studii Cercetari Energet. 11, 325-43 (1961). Data are presented on a process for desulfurization of noncoking coals from the Yiu valley by an air-steam mixt. Conditions are 380°, 1 hr. reaction time, 85:15 steam-air ratio, 27 l./hr. air-flow rate, 204 ml. condensate/hr., 0-1.00 mm. particle size, and 8-10% ash (dry basis). Desulfurization increased greatly between 360 and 390°, but the ash content did not vary, indicating 360° to be optimum. The time was varied between 15 and 120 min., indicating 2 intervals of desulfurization; the optimum reaction time was 30-60 min. The ash content increased at longer times. The air:steam wt. ratio was varied from 10:90 to 40:60 (wt./wt.) at a practically const. flow rate; this did not affect desulfurization to a great extent. The optimum air:steam ratio was 15:85. Particle size was varied from 0.25-1 mm. to 0-3.0 mm. in 0.5-mm. steps; the effect was not pronounced, indicating suitability of industrial size (0-3.0 mm.). A high ash content increased desulfurization and reduced loss by combustion. Under the best conditions, it was possible to obtain 90-5% desulfurization of a coal initially containing ≦2.5% S with a C loss of 4-5%; this is mainly a function of the air:steam ratio. 31 references.

1960

2.21 Process for the destructive hydrogenation of crude oils, tars, and their residues. Willi Oettinger (Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Germany) U. S. 3,073,777 (Cl. 208-59), 17 Feb 1960, Appl. No. 9,167. In a process for the refining and destructive hydrogenation of crude oils, tars and their residues as initial material by reaction with hydrogen in a first stage containing large-surfaced materials and by further reaction with hydrogen in a second stage in the presence of a hydrogenation catalyst and at a temperature of 350°C to 550°C, the pressure in both stages being in a range of about 5 to 700 atmospheres, the improvement which comprises: heating said initial material to a temperature between about 250°C and 350°C; then leading said initial material through said first stage together with about 0.1 to 0.5 normal cubic maters of hydrogen per kilogram of initial material and subsequently through said second stage together with about 0.5 to 1.5 normal cubic meters of hydrogen per kilogram of initial material.

1921

2.22 3460 Tropsch, H., and Schellenberg, A. Formation of methane in the water-gas process. Brennstoff-Chem., vol. 3, 1922, pp. 33-37; Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp.317-329; Chem. Abs., vol. 16, 1922, p. 2022. Vignon's experiments (abs. 3560, 3561, 3562, 3563), on the reduction of CO to CH_4 by means of H_2 in the presence of CaO and Fe, at 900°-1000° have been repeated and only traces of CH_4 found. The presence of 25-30% CH_4 among the products of dry distillation of $Ca(HCOO)_2$ could likewise not be confirmed. Vignon apparently determined CH_4 by difference and did not allow for residual N_2 in the apparatus.

1913

2.23 3562 Vignon, L. Composition of Water Gas. Compt. rend., vol. 156, 1913, pp. 1995-1998; Chem. Abs., vol. 7, 1913, p. 3405. Water gas prepared by conducting H_2O vapor over coke, the ash of which contained 7-8% CaO, contained 3.45% CH_4, whereas water gas from C obtained from sugar, the ash of which contained 0.8% CaO, gave less than 2% CH_4, CO and CO_2 having been removed. Mixing coke with CaO and passing H_2O vapor over the mixture, there were obtained, with 11% CaO at 1000°, 12% CH_4; with 13% CaO at 1000°, 19% CH_4; with 33% CaO, 23% CH_4, CO and CO_2 removed. Following reactions take place: (1) $4CO + 2H_2O = 3CO_2 + CH_4$; (2) $2CO + 2H_2 = CO_2 + CH_4$; (3) $CO_2 + 4H_2 = CH_4 + 2H_2O$.

2.24 3563 Vignon, L. Formation of Methane by Catalysis from Carbon Monoxide and Water Vapor. Compt. rend., vol. 157, 1913, pp.131-134; Chem. Abs., vol. 7, 1913, p.3602. Substances studied as catalyzers were Fe, Ni, Cu, and the oxides of Si, Al, and Mg. The catalyzers were placed in a glazed porcelain tube and heated at different temperatures in the electric furnace, the temperature being taken from the midst of the catalyzer by a Le Chatelier couple. The temperatures at which a maximum yield of CH_4 was obtained and the % present in the resulting gas after deducting CO_2 and CO are as follows: Al_2O_3, 950°, 39.1%; MgO, 900°, 58.7%; SiO_2, 750°, 43.5%; Fe, 950°, 35.5%; Ni, 400°, 89.3%; Cu, 700°, 74.1%. With Fe, Al_2O_3, and SiO_2, carbides are evidently an intermediate product and these carbides, as soon as formed, are acted upon by H_2O vapor with the formation of CH_4: for example, $12CO + 2Al_2O_3 = C_3Al_4 + 9CO_2$; $C_3Al_4 + 6H_2O = 3CH_4 + 2Al_2O_3$. Another explanation for the formation of CH_4 is that under the influence of catalyzers the following reactions take place: $CO + H_2O = CO_2 + H_2$; $3H_2 + CO = CH_4 + H_2O$; $4H_2 + CO_2 = CH_4 + 2H_2O$.

1911

2.25 3560 Vignon, L. Action of Water Vapor on Carbon in the Presence of Lime. Compt. rend., vol. 152, 1911, pp. 871-874; Chem. Abs., vol. 5, 1911, p. 2044. If water vapor is allowed to act upon a mixture of C and CaO at 600°-800°, H_2, CH_4, and some C_2H_4 are formed besides CO and $CaCO_3$. The mixture of CaO and C decomposes H_2O more rapidly and at lower temperature than C alone. Much H_2O and long heating reduce the amount of CH_4 as the latter is decomposed by the H_2O to CO and H_2. The above reactions may explain the formation of marsh gases and natural gases as well as formation of petroleum in nature.

2.26 3561 Vignon, L. Formation of Hydrocarbons from Carbon Monoxide. Bull. soc. schim. (4), vol. 9, 1911, pp. 18-20; Chem. Abs., vol. 5, 1911, p. 1088. CO is converted into CH_4 by conducting CO over a mixture of CaO and $Ca(OH)_2$ at about 400°. The reaction takes place with the intermediate formation of Ca formate, which decomposes to give CH_4 and C_2H_4. This salt at 360°-370° gives a gas containing 20% CO_2, 27% CO, 51% H_2, and 2% hydrocarbons.

ADDENDA

1965

2.27 Effect of incombustible material on critical oxidation temperature of coal. D. K. Nandi, S. C. Banerjee, and R. N. Chakravorty (Central Mining Res. Sta., Dhanbad). Indian J. Technol. 3(5), 160-2 (1965) (Eng). The crossing point (Temp at which a 20-g. sample of fine coal, heated in an oil bath, crosses the bath temp.) increased with increase in ash content in lab. tests on several Indian coals. The rate of increase was enhanced at higher % of ash, esp. at an ash content $> 60\%$. The magnitude of the increase depended in general on the nature of the coal; for most Jharia coals (higher rank) it was 160-170°; but for Ranigunge coal (lower rank), it was usually in the range 120-130°.

2.28 Reaction kinetics of the gasification of carbon with H_2O-H mixtures under pressures. K. Hedden and G. Mienkina (Univ. Muenster, Ger.). Brennstoff-Chem. 46(11). 366-71 (1965) (Ger). Pure C and coke were contacted with H_2O-Ar and H_2O-H-Ar mixts. at temps. from 950° to 1150° and the CH_4 and CO formation measured. The H_2O partial pressures were 5, 12.5, and 25 atm., the H partial pressures ranged from 0 to 50 atm. The total pressure was kept at 50 atm. C particles with a granulation of 0.4-1.0 mm. were used to prevent diffusion. Equations are given for the rates of formation of CH_4 and CO from pure C or coke. The ash content of the coke increases its reaction rate for the formation of CH_4 and CO about 30-40 times. Results obtained with pure C are approx. the same as those obtained with coke at a 150° lower reaction temp.

2.29 The influence of the ash content and ash composition of coals on their coking ability and the properties of the resulting cokes. II. Heinrich Echterhoff, Josef Langhoff, and Werner Peters (Bergbau-Forsch. G.m.b.H., Essen-Dray, Ger.). Brennstoff-Chem. 46(4), 110-17 (1965) (Ger); cf. CA 62, 2638h. The coking characteristics of coals of varying ash contents were detd. Residues from flotation were added to low-ash coals to make charges of predetd. ash content for processing in semi-plant-scale ovens. The mech., phys., and chem. properties of the resulting cokes were detd. These included d., pore vol., reactivity, Fe distribution, and chem. analysis. An unequivocal statement of the effect of the mineral content on the coking process and on the properties of the resulting coke could be made only for coals of the lowest ash content of known compn.

1964

2.30 Effect of ash content and ash composition of coals on their coking capacity and on the properties of the resulting coke. I. Heinrich Echterhoff, Josef Langhoff, and Werner Peters (Forschungsinst. Steinkohlenbergbauvereins, Essen, Ger.). Brennstoff-Chem. 45(10), 306-15 (1964) (Ger). A crude coal with a comparatively high content of volatile matter was sepd. into 6 fractions by a cyclone washer. Various phys. and chem. properties of the 6 fractions were detd. and the results tabulated, e.g., chem. analysis, screen analysis, mineral content, and chem. analysis of the ash. The fractions showed pronounced differences in ash content, ash compn., and total S, but did not differ materially in such properties as volatile matter, elemental analysis, and degassing behavior. The crude coal and the 6 fractions were then subjected to coking under simulated semi-industrial conditions. The water content of every charge was adjusted to 10%, followed by coking at 1100, 1200, and 1300°, resulting in final coke cake temps. of 925, 1000, and 1975°. The coke yield for the fractions did not show great differences and amounted to ~70-71%. The coarse part (> 100 mm.) of the total coke increased with increasing ash content of the starting material. For instance, a fraction with an ash content of 2.3% coked at 1300° gave 35.2% coarse (> 100-mm.) coke, but another fraction with an ash content of 5.7% identically treated gave 76.5% coarse coke. The hardness of the coke obtained was strongly dependent on the ash content, decreasing with increasing ash content in the starting material. The coking temp. had a minor effect on the coke hardness. The chem. analysis of the various cokes did not show big differences; the C and H contents depended on the coking temp. The volatile matter content of the cokes depended on the coking temp., and the S content increased with the total ash. From the chem. properties of the cokes, the reactivity with CO_2 at 1050° was represented graphically; the reactivity increased with increasing ash content, but decreased with increase in coking temp. At a coking temp. of 1300°, the reactivity was almost ash-indepdt. The ash could have a catalytic effect on the gas reactions occurring during coking. Since an ash content of 6% gave optimum coking, it is possible that the ash distribution is important. If the ash exceeds 6%, the C surface for gas reactions is decreased because more and more nonreacting ash is present at the surface. Another possible explanation is a change in the coke structure brought about by the ash. The microporosity of the coke, important in solid-gas reactions such as the C-CO_2 reaction, can be increased by the presence of ash up to a certain concn. If the coking temp. is increased, sintering combined with phase changes in the ash can occur, resulting in a decrease in microporosity in favor of a lower gas reaction promoting coarse porosity.

1962

2.31 Ash content and reactivity of peat coke. N. D. Drozhalina and V. E. Rakovskii. Khim. i Genezis Torfa i Sapropelei, Akad. Nauk Belorussk. SSR, Inst. Torfa 1962, 61-4. There is a definite relation between the types and amts. of ash components and peat-coke reactivity. Higher contents of SiO_2 and Al_2O_3 lower the reactivity while higher percentages of Fe_2O_3, MnO_2, and S compds. tend to increase it. Ash must be present in a very finely dispersed state to exhibit this effect.

2.32 Removing a layer of ash from a catalyst in a hydrocracking process. William B. Retallick (to Consolidation Coal Co.). U.S. 3,275,546 (Cl. 208-108), Sept. 27, 1966, Appl. Dec. 28, 1962; 4 pp. A method of removing a thin outer layer of ash from a catalyst used to catalytically hydrogenate ash-contg. hydrocarbonaceous liquids is described. In the catalytic hydrogenation of coal ext. at 400-550° and 1000-10,000 lb./in.^{2}, a H feed rate of 5-100 ft.^{3}/lb. of feed, and a liquid feed rate of 10-150 lb./hr./ft.^{3} of reactor vol., the catalyst has a size of 1600µ. The velocity of the upwardly flowing liquid (ext. + recycle liquid) is 0.05-1.0 ft./sec. The catalysts are metals of Group VI, e.g., Mo combined with oxide or sulfide of Co or Ni and supported on a hydrous oxide, such as alumina gel. The coal ext. not converted is withdrawn and recycled. The ash on the catalyst is removed by introducing a portion of unconverted ext. into the liquid-phase, dense fluidized bed in the form of a liquid jet (10-30 ft./sec.). The liquid jet causes turbulence in only a portion of the dense fluidized bed. The turbulence is sufficient to cause attrition of the catalyst particles, but is insufficient to disrupt the dense fluidized bed. The ash is removed from the catalyst particles as fines ($<$ 20µ in diam.) and passed out of the hydrocracking zone into the unconverted ext. A portion of ext. is withdrawn from the hydrocracking system to prevent excess buildup of fines.

2.33 Ash removal from coal products. Everett Gorin, Robert T. Struck, and Clyde W. Zielke (to Consolidation Coal Co.). U.S. 3,232,861 (Cl. 208-8), Feb. 1, 1966, Appl. Aug. 22, 1962; 7 pp. The alk. ash (compds. of Na, K, and Ca) is removed from coal ext. by water washing, and the partially deashed ext. is fed to a catalytic hydrogenation process. The remaining ash deposits on the catalyst, and is subsequently removed by abrasion. The alk. ash poisons the catalyst, and cannot be fully removed by abrasion. The inert ash does not affect the catalyst. There was a H consumption of 3.33 wt. % of ext. with an abraded catalyst used with ext. contg. only inert ash vs. 3.09% consumption with abraded catalyst containing alk. ash.

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2.34 Effect of ash content on the rate of reaction of Angren and Moscow coals. G. P. Zybalova and N. N. Dushanova. Nauchn. Tr. Vses. Nauchn.-Issled. Inst. Podzemn. Gazifik. Uglei 1961, No. 5, 13-18. Weighed samples of coal fastened to quartz spirals were heated in a quartz tube in a N stream to 900°; a loss in wt. was observed upon passage of a stream of CO_2. An increase in the ash content of the coal from 14 to 30% decreased the reaction rate with CO_2 by half. The Fe_2O_3 content of the ash influenced the rate of gasification. From Ref. Zh., Khim. 1962, Abstr. No. 8M68.

2.35 Change in ash content and ash composition of coal during chlorination. M. I. Savin and B. S. Vitukhnovskaya. Tr. Dnepropetr. Met. Inst. 1961(44), 61-5. Gas and brown coal ground to 0-0.2 mm. was mixed with a 4-fold amt. (by wt.) of H_2O and treated with Cl at 90°. During the first 3 hrs., the brown coal was 83.7% de-ashed and the hard coal 57.6% de-ashed. Prolonged chlorination decreased the content of Si in the coals; Si is present in the form of organosilicon compds. From Ref. Zh., Khim. 1963, Abstr. No. 2P41.