5. Solvent/Catalyst Interactions

A. Solvent Structure

1974

5.1 Activated extraction of coal using a hydrogen-donor solvent. L. L. Anderson, M. Y. Shifai & G. R. Hill (Univ. Utah) Fuel 53 #1:32-37 (Jan. 1974). Extraction of coal from Spring Canyon Coal Mines (45.7% volatile matter) with tetralin at 47°-87°C was greater with than without ultrasonic energy input, independent of particle size, and greater for lithium/ethylenediamine-reduced coal than for raw coal. The ultrasonic extraction followed second-order kinetics during the first hour and first-order kinetics thereafter. The second-order and first-order enthalpies were 8.7 and 2.5 kcal/mole, respectively, and entropies were -44 and -70 e.u. The ultrasonic energy probably affects the rupture of strong hydrogen or aliphatic covalent bonds which cannot be broken by the solvent alone. Diagram, graphs, tables, and 25 references.

1973

5.2 106671r Role of hydrogen in the process of coal extraction. Rauk, Jerzy; Rutkowski, Marian (Gl. Inst. Gorn., Katowice, Pol.). Koks, Smola, Gaz 1973, 18(3), 77-80 (Pol). The role of H was studied by chromatog. anal. of the products of thermal degrdn. at 400° of the extg. agents and of coal. It involved stabilization by H of free radicals resulting from the thermal degrdn. of coal during its extn. with crude and hydrogenated anthracene oil. The exptl. data are tabulated and discussed in terms of short-chain free-radical processes taking place during extn. Introduction of H into the extn. mixt. results in increasing the degree of coal conversion from 40 to 75% in the pressure range 38-118 atm.

5.3 7757s Uncatalyzed hydrogenation of coal. Liebenberg, Barend J.; Potgieter, Hendrik G. J. (Dept. Ind. Chem., Univ. Potchefstroom, Potchefstroom. S. Afr.). Fuel 1973, 52(2), 130-3 (Eng). The title reaction was investigated in a batch reactor with Tetralin as solvent, the method differing from others mainly in the sampling methods employed. Samples were withdrawn from the reactor after reaction temp. and pressure had been reached, thus excluding effects of heating to reaction temp. and cooling to ambient conditions. Simple series or parallel reactions for the hydrogenation of coal suggested in the literature are oversimplified mechanisms.

1972

5.4 161936k Low-condensation part of the hydrogenation product of lignite vitrinite. Abdurakhmanov, K.; Zabramnyi, D. T. (Inst. Khim., Tashkent, USSR). Uzb. Khim. Zh. 1972, 16(6), 52-4 (Russ). The structural-group compn. of the title product, calcd. by the method of R. N. Hazelwood (1954) from exptl. data on n, d., and mol. wt. agreed well with that detd. by gas chromatog. The expts. were done with vitrinite sepd. manually from Angrenskii lignite. The hydrogenation took place at 380° and 100 atm in the presence of 2% MoS_3 as catalyst and the petroleum ether ext. was studied. The gas chromatog. was done with a 1 m x 4 mm column packed with Chromaton W satd. with 5% Apiezon M. The initial temp. was 100° and the rate of its increase was 5°/min. N was used as the carrier gas. The chromatograms of the product were compared with those from hydrogenation of anthracene, phenanthrene, and pyrene. The av. no. of rings in the product mols. was 4.34, including 3.94 arom. rings.

1971

5.5 138603r Synthetic fuels process. Gorin, Everett; Lebowitz, Howard E.; Rice, Charles H.; Struck, Robert T. (Res. Div., Consolidation Coal Co., Library, Pa.). World Petrol. Congr., Proc., 8th 1971, 4, 43-53 (Eng). Appl. Sci. Publ. Ltd.: London, Engl. A coal liquefaction process is described. The process is an integrated operation with recycle of the natural solvent, generated by ext. hydrogenation, to the extn. step. The extn. behavior of various coals is considered with regard to rank, and the extn. kinetics is discussed.

5.6 81467p Coal liquefaction using high- and low-boiling solvents. Keller, John E.; Hochman, Jack M.; Foster, James Q. (Esso Research and Engineering Co.) U.S. 3,726,785 (Cl. 208/8; C 10g), 10 Apr 1973, Appl. 120,437, 03 Mar 1971; 7 pp. The 1st and 2nd slurries of a particulate coal are formed with low- and high-boiling fractions of a coal-derived solvent boiling at 300-1000°, the cut point of the 2 fractions being from ~500 to ~600°. The slurries are sep. liquefied, producing a higher total cyclohexane conversion of the coal than if the coal had been slurried instead in the total coal derived solvent and liquefied under like conditions. The low boiling coal-derived solvent should contain ≧10.5 wt. % H, and the high boiling coal-derived solvent ≦9.5 wt. % H. Liquefaction conditions include a H treating rate of ~0.1-6 wt. % H (moisture, ash free [MAF]) coal. Liquefaction conditions included a temp. of 700-950° at 300-3000 psig, and a liq. residence time of 5-60 min with a solvent-to-coal ratio 0.8:1 to 2:1. In an example, a slurry of coal was prepd. with each cut at 1.2:1 solvent-to-coal ratio. The cyclohexane conversion of the slurry prepd. from 400-500° F cut was an av. 37.8 wt. % (MAF coal) and that of the slurry prepd. with the 500-700°F cut was an av. 3090 wt. % (MAF coal).

5.7 99786u Thermal liquefaction of a subbituminous coal. Seitzer, Walter H.; Shinn, Robert W. (Sun Oil Co.) U.S. 3,594,304 (Cl. 208-8; C 10g), 20 Jul 1971, Appl. 13 Apr 1970; 2 pp. The title process is accomplished by subjecting the coal to soln. in a hydrogenated polycyclic-compd. solvent under H pressure (2000-3000 psig) at 440-50° for a 5 to 20 min residence time. The solvent to coal ratio is 2:1. Such solvents as Tetralin, dihydronaphthalene, dihydrophenanthroline, dihydroanthracene, and several others are used in the process. The resulting product is similar to crude oil and is subjected to the usual refining techniques.

5.8 61648h Effect of the degree of hydrogenation of extracting agents on the yield and quality of coal extracts. Rauk, Jerzy; Rutkowski, Alojzy; Rutkowski, Marian (Glowny Inst. Gorn., Pol.). Koks, Smola, Gaz 1971, 19(11), 308-11 (Pol). Coal samples were extd. with crude anthracene oil (I) contg. 5.15% H, with hydrogenated I contg, 5.42, 6.72, or 7.04% H, and with hydrogenated coal exts. contg. 7.07% H. Thus, 180 g coal of particle size ≤0.5 mm and 450 g oil were heated in an autoclave under N at 400 and 420° for 30, 70, and 90 min. With increasing H content of the extg. oil, the amt. of ext. increased from 8.8 to 67.5% and the amt. of the C_6H_6-insol. matter in these exts. decreased correspondingly from 22.39 to 7.73%. During hydrogenation of I with H over 20% WS at 410-40° and 200 atm., the fraction b. $>$ 445° is decreased from 51 to 5-9% and that b. $<$ 445° is increased from 48.4 to 91-94.9%. The latter is responsible for the extractive power and selectivity of the oil.

5.9 101991y Hydrogenation of coal extracts. Rauk, Jerzy; Rutkowski, Alojzy; Rutkowski, Marian (Gl. Inst. Gorn., Pol.). Koks, Smola, Gaz 1971, 19(12), 325-9 (Pol). Coal from 2 Polish mines was extd. with a mixt. of hydrogenated anthracene oil and the circulating oil from hydrogenation of another coal ext. Extn. was performed for 30 min at 400°/100 atm. These exts. were hydrogenated together with the extg. medium at 400-40°/200 atm with electrolytic H over a W-contg. catalyst (20% WS_2) on an aluminosilicate carrier. This app. described permits operating at ≤500°/≤300 atm. Good hydrogenation effectiveness was obtained only by repeating the operation. J. Brzezinski.

5.10 Hydrogenation of solid fuels. A. A. Krichko (Inst. Fossil Fuels) K T T #2:31-39 (1971). A review of literature for the period 1927-69, with 49 references, includes the author's unpublished research on hydrogenation of Kuzbass gas coal plus a petroleum fraction b. above 240°C with and without free radical type polymerication inhibitors (anthraquinone, anthracene, etc.) at 425°C and 100 atm of hydrogen to convert 90-93% of the organic matter of the coal (OMC) in the presence of catalysts. Without catalyst the conversion is 17.7%, but rises to 67% with addition of 1% molybdenum applied by impregnating the coal with ammonium molybdate. A major part of the molybdenum may be replaced by trivalent iron. With 0.2% Mo and 1% Fe^{2+} (calculated on OMC) the conversion rises to 82.7%. Further decrease of molybdenum cannot be compensated by iron. The beneficial effect of combined catalyst metals in Indian coal hydrogenation has been reported by D. K. Mukherjee, et al (Symp. on Chem. and Oils from Coal, Dhanbad, Dec. 1969). Conversion of the petroleum products in the coal-oil mixture is likewise improved. At 425°C and 100 atm, from the 240°C ibp fraction with a sulfur content of 3.4%, 52% of the sulfur is removed as H_2S in coal-oil hydrogenation and only 27.5% without coal; the formation of saturated hydrocarbons is reduced to one-half, and the yield of liquid products increases from 80-85% to 93-95%. In hydrogenation of coal with a similar fraction contg. only 1.6% sulfur, the OMC conversion fell by 10-12%. The reasons probably are: (1) sulfur compounds, because of high electron affinity of sulfur, tend to react more readily with unstable radicals from coal destruction than do hydrocarbons; and (2) high molecular hetero compounds are dehydrogenated more easily. The experimental data obtained show that 75-80% conversion of coal under the above conditions is feasible with a solvent which is free from naphtha and ligroin fractions. Higher conversion, without raising the pressure or using excessive amount of catalyst, is obtainable by adding to the reaction 1-5% of anthraquinone, anthracene as inhibitors, to give up to 92-93% conversion of OM in gas coal and 95-90% in the case of brown coal. The anthracene remains practically unchanged. Addition of 1% of ionol cut down the conversion from 75-80% to 20-23%. Having mobile hydrogen atoms in 9- and 10 positions, anthracene provides a reactive radical which is capable of migrating into the micropore system of the coal and thus stabilizing the disintegration products to prevent their recombination before hydrogenation. Ionol on heating provides reactive phenoxy radicals to aid in dehydrogenation of structural units and the formation of high molecular polycondensed fragments. Coal-oil hydrogenation offers savings in external hydrogen consumption. The 5-6% of hydrogen required for 95-97% conversion include only 1.52% from a foreign source, because most of the hydrogen is supplied by the petroleum product.

5.11 78930w Crosslinking of an organic coal mass. Gadyatskii, V. G.; Shapiro, M. D.; Belozerov, A. M. (Dnepropetr.

Khim.-Tekhnol. Inst., Dnepropetrovsk, USSR). *Khim. Tverd. Topl.* 1971, (3), 54-9 (Russ). The crosslinking of linear mols. of coal matter, taking place at 170-200° under the action of the crosslinking agents ω-hexachloro-p-xylene (I), 9,10-bis (chloromethyl)-anthracene (II) and N-4-dinitroso-N-methylaniline (III) is indicated by a decrease in the yield of volatile matter and of semicoke tar, by the soly. in phenanthrene (IV) and acenaphthene (V), and by the loss of the sintering and plasticizing properties. Samples of gassy, high-volatile fatty, and coking coals ground to 0-0.25 mm were heated at 170-230° in N during 1 hr. I, II, and III were added in amts. of 3-5% to the coal samples. The crosslinking mechanism is discussed. Coking of briquets prepd. at 100° under 100 atm with 9% anthracene (VI), IV, and V resulted in a 7-10% increase in the coke yield and in avoidance of swelling and flow of the briquets during coking in the case of IV, and in an increase in the coke yield of 1% with swelling in the case of V. The effects are explained by the crosslinking action of VI, the plasticizing action of IV and interaction of V with the coal mols. without crosslinking.

1970

5.12 74625q Solvent extraction of coal by a heavy oil. Gatsis, John G. (Universal Oil Products Co.) U.S. 3,705,092 (Cl 208-8; C 10g), 05 Dec 1972, Appl. 99,704, 18 Dec 1970; 2 pp. Carbonaceous material, such as coal, is converted to liq. products by solvent extn. with a heavy carbonaceous liq. contg. C_7H_{14}-insol. material, such as a heavy asphaltene-contg. crude oil. The admixed solvent and solid are heated to 55-935°F 500-1000 psig in the presence of H to liquefy the desired fraction of solid. The mixt. of solvent and liquefied coal recovered as the product boils at $>\sim$650°F, and has a reduced asphaltene content.

5.13 111673y Solution hydrogenation of lignite in coal-derived solvents. Severson, D. E.; Skidmore, D. R.; Gleason, D. S. (Dep. of Chem. Eng., Univ. of North Dakota, Grand Forks, N. Dak.). *Trans. AIME* 1970, 247(2), 133-6 (Eng). A modified Pott Broche process was used to produce, in lab. quantities, liq. products by soln. hydrogenation of coal. Over 100 lignite soln.-hydrogenation runs were made in a 1-gallon stainless-steel autoclave provided with stirring. The solvents included anthracene oil, lignite tars, Tetralin, *p*-cresol, and others. Optimum operating conditions were 750°F and 1500 psig initial H pressure, corresponding to ~3200 psig max. pressure in the app. Anthracene oil would be the most promising com. material for starting solvent use. It performed well for 5 successive cycles of reuse in batch runs. Lignite tars decompd. under reaction conditions.

1969

5.14 51908a Extraction of naphthalenes from middle distillates. Riad, M. A.; Mahmoud, B. H.; Hafiz, M. Yl; Abdou, I. K. (Petrol. Sect., Nat. Res. Center, Cairo, UAR). J. Inst. Petrol., London 1969, 55(543), 168-73 (Eng). The use of furfural, PhOH, aniline, morpholine and p-cresol as selective solvents for the extn. of dicyclic aromatics present in a 200-50° petroleum fraction were compared, under identical conditions of extn. A general trend was observed in that the addn. of water improved the selectivities of most solvents tested, for monocyclic aromatics, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. Water-satd. p-cresol was poor in selectivity for both naphthalene and its Me derivs.

5.15 4993k Solvent extraction (at BCURA industrial laboratories, Leatherhead). Bond, Raymond L.; Ladner, William R. Chem. Ind. (London) 1969, (39), 1366-7 (Eng). A flow sheet for the solvent treatment of coals is given, and methods for further processing of the ext. are examd. The highest extn. yields are obtained from high and medium volatile coals. The possible production of 9,10-dihydroanthracene and current processing studies of various types of C as substitutes for petroleum coke or graphite are briefly discussed.

5.16 114111v Hydrogenation-solvent extraction of coal. Corey, Richard S.; Gleim, William K. T.; Riedl, Frederick J.; Sunagel, George R. (Universal Oil Products Co.) Ger. Offen. 2,040,764 (Cl. C 07c, C 10g), 18 Mar 1971, U.S. Appl. 18 Aug 1969; 33 pp. Coal was converted by H treatment into liq products by using a double selective solvent system, whereby nonconverted coal and ash was sepd. without filtration. Thus, 100 g bituminous Pittsburgh bed coal of 0.15 mm particle size was mixed with 300 g Tetralin and milled 5 hr to give a colloidal coal mixt. with particles < 0.1 mm diam and 95% $< 2\mu$ diam. coal particles. The colloidal mixt. was heated at 430°, 140 kg/cm^2 H pressure, 0.5 hr contact time, and 113 std. m^3:0.159 m^3 H-coal ratio and Tetralin removed to give a liq. product of mol. wt. 503 and contg. H 7.18, C 87.70, and solids (coal, ash, etc.) 0.50%. The liq. product (1 part) was extd. with 5 parts C_6H_6 1 hr at 120° to give a H-rich upper and a H-poor C_6H_6 phase. The liq. coal product removed from the upper phase contained 7.75% H, had 450 av. mol. wt., and was practically free (0.01%) from solids. The lower phase had 1150 av. mol. wt. and contained practically all the solids present in the original extn. product.

5.17 115004n Interaction of coals with solvents. Shapiro, M. D.; Gadyatskii, V. G. (Dnepropetrovsk. Khim.-Tekhnol. Inst., Dnepropetrovsk, USSR). Khim. Tverd. Topl.

1969, (4), 142-8 (Russ). A concentrate of grade Zh Donets coal was treated with anthracene, phenanthrene, and dimethylnaphthalenes at 230, 260, and 290° for periods up to 17 hrs. and solvent-coal ratio 10:1. The percentages of residual and dissolved coal were detd. and also the volatile content and caking capacity of the residual coal. By treatment with anthracene, the materials balance at all temps. and times of treatment exceeded 100%. The residual coal was deficient in caking capacity and content of volatiles. Structurization of the linear and branched components of the macromols. of the original coal occurred with accumulation of crosslinked, steric macromols. With phenanthrene, the materials balance exceeded 100% only at higher temps. and longer periods of treatment. The residual coal was little changed in caking capacity and content of volatile matter. Phenanthrene dissolved linear and branched components of the macromols. of coal and interacted with them, whereby certain of their properties were changed, but not their structure. With dimethylnaphthalenes, the materials balance was always $<$ 100%, and the residual coal was similar to the original coal. No interaction of solvent with coal occurred in this case.

1968

5.18 33395p Coal liquefaction using dual solvent extraction. Corey, Richard S.; Riedl, Frederick J.; Campbell, Douglas R. (Universal Oil Products Co.) U. S. 3,535,224 (Cl. 208-8; C 10g), 20 Oct 1970, Appl. 25 Jun 1968; 4 pp. A solvent-extn. process is described for producing H-enriched hydrocarbonaceous products from particulate coal. The coal is treated with a polycyclic aromatic solvent, such as Tetralin, and a secondary solvent, such as dichloronaphthalene, and H at 250°-500° and ~ 2000 psig. About 50 wt. % of the coal is converted to liq. coal extract having the following comp.: S 0.72, benzene insol. 8.04, and H 7.07 wt. % and a mol. wt. 396. Stanley J. Gasior.

5.19 128791r Dissolving solid carbonaceous material. Martin, Terence Geoffrey; Wise, William S. D. (Coal Industry [Patents] Ltd.) Brit. 1,287,570 (Cl. C 10b), 31 Aug 1972, Appl. 61,651/68, 30 Dec 1968; 4 pp. A cyclic process was developed for extg. sol. or solubilized matter from coal or like carbonaceous materials with a reactive solvent at 360-425° to form a soln. or ext. of coal along with recovery of the solvent, including the reacted solvent and (or) the solvent produced in the extn., from the soln. or ext. of coal. The recovered solvent is used again as the reactive solvent to form further solns. or exts. of coal. The improvement is comprised of adding to the recovered solvent a cyclic activator, a compd. having either at least 2 carbocyclic rings or a heterocyclic ring having N as the heteroatom and which is capable of dehydrogenation, such dehydrogenation giving rise to an aromatic ring rearrangement, or a compd. having N in an aromatic ring, whereby the soly. or solubilizability of the sol. or solubilizable matter of the coal in the recovered solvent is enhanced. The cyclic activator is a cyclic nitrogeneous compd., e.g. 1,2,3,4-tetrahydroquinoline, indoline, indole, pyrrolidine, pyrazine, piperidine, perhydrophenanthrene and 9,10-dihydroanthracene. Examples using several of these activators were given (esp. 1,2,3,4-tetrahydroquinoline). The wt. ratio of cyclic activator is usually 3-5%. The wt. ratio of solid carbonaceous material is usually 2:1 up to 5:1 or higher.

1967

5.20 92630q Solvation of coal. Willard C. Bull, Lawrence G. Stevenson, Dean L. Kloepper, and Thomas F. Rogers (to United States Dept. of the Interior). U.S. 3,341,447 (Cl. 208-8), Sept. 12, 1967, Appl. Jan. 18, 1967; 6 pp. A process for upgrading of carbonaceous fuels by a soln. process into low-ash, low-O, and low-S fuels is described. Thus, Kentucky no. 11 coal was dissolved in a solvent recovered from previous extn. runs (b. 150-750°, d. 1.1, C:H 1.0/0.9 to 1.0/0.3) at 1000 psi. (80% H), 410°, and solvent/coal ratio 3/1. The solvent/coal slurry was heated in 12-20 sec. to 410° until the viscosity rose and then dropped to 3.43. The properties of the product, after filtering, were 0.48% ash, 36.6% volatile matter, 220° m.p., d. 1.24, and 15,768 BTU./lb.

1966

5.21 Kinetics and mechanism of solution of high volatile coal. George R. Hill, Hassan Hariri, R. I. Reed, and Larry L. Anderson (Univ. of Utah, Salt Lake City). Advan. Chem. Ser. No. 56, 427-46, discussion 446-7 (1966) (Eng). A kinetic study of the dissoln. of a Utah high-volatile bituminous coal in Tetralin was conducted. Equipment for obtaining rate data during the early stages of the reaction were developed. The data are interpreted in terms of a pseudo 2nd-order rate const., av. heats of activation, and apparent entropies of activation; the numerical values of these functions depending on the degree of extn. The rate of soln. in Tetralin of this coal was not an equil. phenomenon, but was a kinetically controlled reaction in which the av. activation energy increased as the reaction proceeded.

5.22 39829g Mechanism of hydrogen transfer to coal and coal extracts. G. P. Curran, R. T. Struck, and E. Gorin (Consolidated Coal Co., Res. Div., Library, Pa.). Amer. Chem. Soc., Div. Fuel Chem., Preprints 10(2), C-130--C-148 (1966) (Eng). The kinetics of coal extn. and of the transfer of H from Tetralin to bituminous coal and a "shallow" ext. derived from coal were examd. expt. A no. of other active H-donor solvents were also tested, such as cyclohexylphenol, cyclohexanol, dihydrophenanthrene, and isopropanol. All of the above donors gave about the same amt. of H transfer at equal time and temp. conditions. A limiting value of the amt. of H that could be transferred was approached at long treatment times. The depth of extn. was a function primarily of the amt. of H transferred and relatively independent of the solvent compn. employed. The H-transfer results were interpreted in terms of a free-radical mechanism wherein the rate-detg. step is the rupture of covalent bonds. The exptl. data could be adequately represented by a model where bonds of 2 different strengths are involved. The dependence of H-transfer rate on Tetralin concn. was quite complex and could not readily be interpreted in terms of a simple theoretical model. A semi-empirical correlation is given which adequately represents the data.— Hydrogen-transfer process to coal and coal extract. George P. Curran, Robert T. Struck, and Everett Gorin (Consolidation Coal Co., Library, Pa.). Ind. Eng. Chem., Process Des. Develop. 6(2), 166-73 (1967).

5.23 Phenanthrene extraction of bituminous coal. Laszlo A. Heredy and Paul Fugassi (Carnegie Inst. of Technol., Pittsburgh, Pa.). Advan. Chem. Ser. No. 55, 448-58, discussion 458-9 (1966) (Eng). Three bituminous coal samples were extd. at 350° with phenanthrene (labeled in 1 series with ^{3}H, in another with ^{14}C). The ext. yield was 80-90%. Converting coal to sol. products breaks C-H bonds; 10-15% of the H content of the coal exchanged with that of the phenanthrene during extn.; 3-8% chem.-linked phenanthrene was found in the exts.; < 1% H exchange took place between pure model compds. (anthracene, p-benzylphenol) and phenanthrene ^{3}H under similar exptl. conditions. Thus, chem. reactions take place during phenanthrene extn. of bituminous coals. The role of phenanthrene in this process is probably an interaction with the free radicals formed in the thermal decompn. of coal.

1965

5.24 Structure determination of pitch resin by catalytic dehydrogenation. C. Karr, Jr., K. B. McCaskill, and J. J. Kovach (Morgantown Coal Res. Center, Bur. of Mines, Morgantown, W. Va.). Fuel 44(6), 437-41 (1965) (Eng). A structure detn. of the C_6H_6-sol., Et_2O-insol. pitch resin from a low-temp. bituminous coal tar was made by catalytic dehydrogenation in pure phenanthridine, acridine, fluoranthene, and p-terphenyl, and by examn. of the ir and uv spectra of the dehydrogenates. Some of the structural features indicated for the original resin were alc. OH groups of a type readily converted to anthrone or quinone ketone groups by dehydrogenation, and naphthenic rings, partially substituted with OH and Me groups, attached to aromatic rings with a considerably higher degree of substitution. Dehydrogenation of these naphthenic rings resulted in a great increase of 3 or 4 atoms on aromatic rings compared to 1 and 2 H atoms.

5.25 The hydrogenation of bituminous coal with α-pipecoline. C. Kroeger and Fr. Burges (Tech. Hochsch., Aachen, Ger.). Brennstoff-Chem. 46(2), 34-6 (1965) (Ger). Bituminous coal of high gas content was hydrogenated with α-pipecoline at various temps. The optimum temp. and time were 315° and 9 hrs. (90.6% coal extd.). The reaction products were recovered by fractional distn. and the following products were obtained from 100 g. coal: gas 0.35, fraction b. 190-360° (20 torr) 43.8, distn. residue 43.9, C residue 9.15, PhOH 0.56, water 2.11 g.

1964

5.26 Theory of the formation of a plastic mass and the caking of coals. G. K. Petrik. Koks i Khim. 1964(5), 1-6. The transition of coals to a plastic state is pictured as a process of thermal decompn. at the weakest bonds of the macromols. representing the org. matter of the coal, leading to the formation of 2 types of materials: (1) low-mol.-wt., low-melting fragments of the macromols., and (2) high-mol.-wt. remnants of the macromols. and products of their condensation. The plastic state in the coking process depends on the interaction of these 2 types of materials. The varying response of various kinds of coals, such as brown coals, long-flame coals, gas coals, lean coals, and anthracite to plasticization in the coking process is reviewed in its relation to the varying degrees of carbonization of the coals resulting from 2 different processes: (1) sepn. of O groups from the macromol., resulting in a decrease of structural hardness, porosity, and an increase of plasticity; and (2) condensation processes. The formation of a plastic mass and its quality depend to a large degree on the coking conditions. Coking under gas pressure contributes to greater plasticity by preventing the escape of low-mol.-wt. products. Application of mech. pressure makes possible plasticizing of coals that are not caking in conventional coking processes. Various degrees of plasticity can be produced by varying the speed of the coking process. Materials that may serve as plasticizers must meet the following 3 requirements: (1) relatively low mol. wt., (2) compatibility with the high-mol.-wt. products of coal thermolysis, and (3) ability to survive the plasticizing temp. range of a given coal in the intramol. spaces of the high-mol.-wt. thermolysis products of the coal. Plastometric expts. with the addn. of 10% of 10 plasticizers to 5 different coals showed the varying effectiveness of the plasticizers and the selectivity of their effect. The selectivity was esp. pronounced in anthracene. The properties of coke with the addn of various plasticizers were also detd. In principle, the mechanism of the interaction of both low- and high-mol.-wt. products of coal thermolysis with the org. caking additives is identical to that of the plasticizing of polymers.

5.27 Thermal conversions of coal in high-boiling organic solvents. E. S. Serik and M. N. Naboka. Sb. Nauchn. Tr. Ukr. Nauchn.-Issled. Uglekhim. Inst. 1964(15), 57-60 (Russ). An app. and procedure for studying thermal conversions of coals in high-boiling org. solvents (anthracene, phenanthrene, naphthalene) are described. The procedure makes it possible to achieve a material balance in the entire expt. as well as sep. for the solvent and products of thermal coal conversion; to det. the dynamics of changes in the activity of a solid residue as a function of temp., time of residence of the coal at a given temp., and the degree of coal metamorphism; to completely sep. the solid and liquid phases formed during the heating of coal; and to study the compn. of the liquid phase. From Ref. Zh., Khim. 1964, Abstr. No. 23P62.

1963

5.28 97359p Deashing coal in the absence of added hydrogen. Ward J. Bloomer (to Lummus Co.). U. S. 3,375,188 (Cl.208-8), March 26, 1968, Appl. Nov. 26, 1963, and Dec. 19, 1966; 5 pp. A method is described for producing substantially ash-free coke from coals selected from bituminous, subbituminous, and lignite contg. extractable carbonaceous matter, fusain, and mineral matter. There is salvage of gas, aromatic solvents, oils and NH_3. The method comprises mixing the coal in crushed form in the absence of added H with a high-boiling aromatic liquid solvent having cut points, converted to 1 atm., of 600-900°F. to form a soln. of the extractable carbonaceous matter in which solids including insol. fusain and mineral matter are suspended. The suspended solids are sepd. from the soln. after it has been cooled to 400-700°F. The ratio of solvent to coal is 1:1 to 3:1, but may be a wider range of 0.5:1 to 6:1. The temp. of 600-850°F. is maintained in the soln. for 3-120 min.

1962

5.29 Catalytic dehydrogenation of coal. Raphael Raymond, Irving Wender, and Leslie Reggel (U. S. Bur. Mines, Pittsburgh, Pa.). Science 137, No. 3531, 681-2 (1962). Vitrains from 5 different sources, together with 3 related materials, were refluxed with Pd, Ru, and Rh catalysts in high-boiling aromatic and heteroaromatic solvents. As much as 53% of the H in 1 vitrain was evolved as H gas. The yield of H varied with the rank of the coal and the nature of the solvent, but was little influenced by the metal or the catalyst support.

1961

5.30 Hydrocracking of the high-boiling fraction of coal tar on a stationary-bed catalyst at 30 atmospheres. Ya. R. Katsobashvili, Yu. N. Garber, E. I. El'bert, and Z. G. Belenko. Koks i Khim. 1961, No. 10, 48-52; cf. CA 51, 16321g; 54, 10293h; U.S.S.R. 113, 353, CA 53, 4718a.---Hydrocracking of high-boiling fractions of coal tar, b. 270-360° plus, under 30 atm. at 400-700° over active hydrocracking catalysts brings about a large conversion of the semicondensed aromatic components to C_6H_6, PhMe, xylenes, and naphthalene with its methylated homologs. For the most complete conversion, the issuing products should be recycled in the limits of 60-200%. By choosing the optimum catalyst and operating conditions, it is possible to regulate the process to obtain either naphthalene or C_6H_6--PhMe; the former, because of more complete conversion of the raw feed, is more profitable.

1959

5.31 116273z Coal solvation with nonhydrogenated solvent in the absence of added hydrogen. Ward J. Bloomer and Samuel W. Martin (Beverly B. Martin, administratrix) (to Lummus Co. and Great Lakes Carbon Corp.). U.S. 3,379,638 (Cl. 208-8), April 23, 1968, Appl. Aug. 3, 1959, and Jan. 25, 1965; 6 pp. A substantially ash-free soln. of carbonaceous matter is prepd. from bituminous and subbituminous coal and lignite which consist of extractable carbonaceous matter, fusian, and mineral matter. The process comprises mixing the coal in crushed form with a nonhydrogenated, high-boiling liquid solvent of high aromaticity. Its boiling temp., converted to 1 atm., ranges from 650 to 850°F. The mixt. is heated in the absence of added H to a temp. of 600-850°F. to form a soln. of the extractable carbonaceous matter wherein solids, including fusain and mineral matter, are suspended. The suspended matter is sepd. from the soln. A temp of 750-825°F. and above the final decompn. temp. of the initial coal is preferably maintained in the solutizer. The heating of the mixt. is performed under a pressure of 1-8 atm. A ratio of high-boiling liquid solvent to raw coal of ~ 2:1 to 3:1 is preferred, however a ratio range of 0.5:1 to 6:1 may be used. The soln. is cooled to 400-700°F. prior to sepg. the suspended solids from the soln.

5.32 Mechanism of the action of diluting components in a charge (during coking). V. E. Rakovskii. Khim. Pirogen. Protsessov, Inst. Torfa Akad. Nauk Belorussk. SSR, Mosk. Torf. Inst. 1959, 188-90; cf. preceding abstr. The addn. of solid, infusible substances, and esp. active substances of an aromatic nature, increases the mean mol. wt. of the portion of the charge capable of reaction, and this shortens the time required for the formation of a dense aromatic lattice. The addn. of chem. active aromatized coke with a large surface area results in increases in condensation reactions and in the interaction of this solid portion with the low-mol.-wt. aromatic compds. Naphthenes play an important role in the coking of fuel rich in H. The dehydrogenation of these compds. by O-contg. substances at the start of the decompn. has a favorable effect on the formation of a stable coke because of the increase in aromatic compds. The mechanism of the action of added aromatic hydrocarbons on poor, strongly carbonized, non-caking fuels and of added semicoke and coke on fuels rich in volatile substances is based solely on the chem. nature of both processes. The addn. of anthracene oil to highly carbonized fuels that have lost the capacity to be transformed into a plastic state results in swelling of the high-mol.-wt. aromatic part of the fuel. The introduction of 2-4% aromatic hydrocarbons greatly increases the stability. The aromatic-compd. oils should have a high b.p.

1958

5.33 Extraction of natural and oxidized coals of the Irkutsk Basin with organic solvents. V. V. Tuturina. Trudy Irkutsk. Gornomst. Inst. 1958, No. 16, 247-56.---The solubilities of 5 typical humus coals in alc., C_6H_6, pyridine, PhOH, and anthracene oil were detd. both before and after oxidn. with 2N HNO_3. Solubilities of the natural coals were rather high and reached 100% in anthracene oil. Oxidized coals were more sol. than natural coals. High-S coals were more sol. than low-S coals.

B. Catalysts, With or Without Solvent

1973

5.34 Preparation of fuels and chemical products from mixtures of coal and petroleum. A. D. Krichko and M. K. Yulin (Inst. Fossil Fuels). KH T T #6:75-80 (1973). A combination process is proposed for producing commercial products from distillates with 320°C ebp derived in the liquid phase hydrogenation of a coal-oil mixture (presumably in the presence of catalyst previously reported by Krichko). The process includes distillation into two fractions and boiler fuel > 320°C, separation of phenols, hydrofining the 240°-320°C fraction, distillation to recover naphtha of 180° ebp for hydroforming and a 180°-320°C fraction for hydrocracking to make gasoline. Tables. Contains new references to 1) A. A. Krichko, T. A. Titova, et al. Trudy IGI 27 #1:111 (1971), 2) A. A. Krichko, R. A. Konyashina, T. S. Nikiforova, T. A. Titova, Trudy IGI 25 #3:123-8 (1971).

5.35 Chemical composition of liquid products from coal hydrogenation. E. A. Dembovskaya, A. A. Krichko, T. A. Titova, D. P. Pchelina, T. M. Ravikovich and M. A. Chubarova (Inst. Fossil Fuels). Kh T T #5:84-90 (1973). Joint hydrogenation of coal and petroleum products at the Institute of Fossil Fuels was conducted in a continuous laboratory apparatus with a reactor of 3 l. volume, at 100 atm and 420-425°C in the presence of 1% trivalent iron and 0.2% molybdenum as catalyst. The composition of the 180° ebp, the 180°-240°, and the 240°-320°C fractions was determined. Thirty-eight aromatics ranging from C_8-C_{10} through diphenyl were identified.

5.36 94543k Catalytic dehydrogenation of coal. 7. Effect of some catalyst variables. Reggel, Leslie; Wender, Irving; Raymond, Raphael (Pittsburgh Energy Res. Cent., Bur. Mines., Pittsburgh, Pa.). Fuel 1973, 52(3), 162-3 (Eng). Bruceton vitrinites were catalytically dehydrogenated at 346° for 5 hr in the presence of phenanthridine; the yield of H was found to be not greatly affected by the catalyst support ($CaCO_3$ or Al_2O_3) or the concn. (10-30%) of metal on the support, but the metal used (Pd, Ru, Rh, Ir, Pt, Re, Fe, Co, or Ni) had a large effect. Pd gave the highest yield of H: ~ 30 H atoms/100 C atoms in the coal.

1972

5.37 Hydrogenation of solid fuel. Effect of quality of coal and of the method of catalyst application. A. A. Krichko,

T. A. Vitova, et al. Kh T T #4:70-75 (1972). Six samples of low-sulfur coal and a sample of brown coal, in the form of a paste with a petroleum fraction b. above 240°C and an anthracene fraction in 40:60:5 ratio, were hydrogenated in a rotary autoclave at 425°C and 50 atm hydrogen pressure for 2 hr in the presence of 0.2% Mo + 1% Fe^{3+} catalyst. The catalyst was applied onto the comminuted coal by successive impregnation with solutions of ammonium molybdate and iron sulfate and subsequent drying to 1-1.5% moisture, or by addition of dry salts to coal. Conversion of the organic matter of coal (OMC) ranged from 74.2 to 92.1%. Optimum yield of liquid products was 86.7-88%, including 23.6-29% originated from coal. However, these results apply only to coal fresh from the mine and are significantly lower for oxidized coal after 30-40 days storage in open air. They were obtained at pressures only one-half of those previously used in the coal hydrogenation industry and with moderate hydrogen consumption. The catalyst application method is very important: with catalyst powder added to coal, conversion of OMC into liquid declines by a factor of 1.6, compared with the impregnated catalyst. With impregnated catalyst, the yield of phenols is 1.5 times and of nitrogen bases 3 times higher. The use of 2%- or 5%-solutions and changes in the coal-to-solution ratio had no significant effect on coal conversion. Yet, a 4:1 ratio gives a higher yield of phenols and nitrogen bases boiling up to 300°C, presumably because more uniform distribution of catalyst is favorable to hydrogenation of the decomposition products in the initial stage of conversion so that they remain in the liquid. The composition of products of 180°-300°C range, at all coal-oil ratios is 7.8% phenols, 8-9% nitrogen bases, and 50-52% aromatic hydrocarbons. Contains reference: A. A. Krichko, R. A. Konyashina, et al. Trudy IGI 27 #1 (1971).

1971

5.38 156541g Effect of ferric oxide on the hydrogenation of Oyubari coal in Tetralin as the reaction medium. Fujiwara, Nobuaki; Matsuo, Akira; Demuratani, Takayuki; Yoshimura, Futoru (Univ. Osaka Prefect., Sakai, Japan). Nenryo Kyokai-Shi 1971, 50(12), 910-18 (Japan). In the presence or absence of Fe_2O_3, Oyubari coals (< 100-mesh), exte. at 50° with pyridine and deashed, were hydrogenated for 1 or 8 hr at 300-400° and 50 kg/cm^2 initial H pressure. Fe_2O_3 suppressed the hydrogenation, and its addn. (100 wt. % to coals) also increased the O content of the hydrogenated (1 hr) coals. On the other hand, Fe_2O_3 was reduced to ferrous ions or metal during the hydrogenation, but these had no tendency to promote the hydrogenation. The aromatic H/C ratio of the hydrogenated coals was nearly the same as that of the original coals, but the aliphatic H/C value increased.

1970

5.39 122241g Interaction of solvent and catalyst in coal hydrogenation. Pastor, G. R.; Angelovich, J. M.; Silver, H. F. (Chem. Eng., Univ. Wyoming, Laramie, Wyo.). Ind. Eng. Chem., Process Des. Develop. 1970, 9(4), 609-11 (Eng). The effect of interaction between catalyst and solvents on the extent of the liq.-phase coal hydrogenation was examd. A subbituminous Wyoming coal was impregnated with varying amounts of ferrous ion catalyst and hydrogenated at 400°. Three solvents were used. Differences in the conversion levels attributable to the solvents decreased as the concn. of the catalyst on the coal increased to 1.0 wt. %. Further increases in catalyst concn. had little effect on conversion. Even when ferrous ion catalyst is used, the soly. characteristics of the solvent (measured by the nonpolar soly. parameter) are important in obtaining max. yields of C_6H_6-sol. products. Coal size is not important.

1967

5.40 30666j Coal hydrogenation. I. General Report. Silver, Howard F. (Univ. of Wyoming, Laramie, Wyo.). U. S. Clearinghouse Fed. Sci. Tech. Inform., PB Rep. 1967, PB-178848, 40 pp. (Eng). Avail. CFSTI. From U. S. Govt. Res. Develop. Rep. 1968, 68(18), 82. The work completed during the 2nd extension of this project has been directed primarily toward evaluating the effect of the concn. of ferrous ion catalyst on the yields and properties of hydrogenated coal bitumen. A complete set of the data obtained is included in Part II of this report.

30667k Coal hydrogenation. II. Test data, notes, and calculations. Silver, Howard F. (Univ. of Wyoming, Laramie, Wyo.). U. S. Clearinghouse Fed. Sci. Tech. Inform., PB Rep. 1967, PB-178849, 51 pp. (Eng). Avail. CFSTI. From U.S. Govt. Res. Develop. Rep. 1968, 68(18), 82. All test data, pertinent notes, and applicable calcns. from the coal hydrogenation study are presented.

30668m Coal hydrogenation. III. Summary report. Silver, Howard F. (Univ. of Wyoming, Laramie, Wyo.). U. S. Clearinghouse Fed. Sci. Tech. Inform., PB Rep. 1967, PB-178850, 5 pp. (Eng). Avail. CFSTI. From U. S.Govt. Res. Develop. Rep. 1968, 68(18), 82. A satisfactory bitumen product can be produced from low-rank coals, such as those found in Wyoming by using a coal-derived solvent such as would be produced as a by-product in a coal hydrogenation process.

1965

5.41 Hydrogenation of coal in the batch autoclave. C. O. Hawk and R. W. Hiteshue (U. S. Bur. of Mines, Pittsburgh, Pa.). *U. S., Bur. Mines, Bull.* No. 622(3), 42 pp. (1965) (Eng). Bituminous coal was tested by a dry method, charging the autoclave with dry ingredients only: coal, catalyst, and H. Sn catalysts showed the highest activity in the widest variety of forms and were the easiest to disperse. As a group, metal naphthenates were the most effective.

1964

5.42 Hydrogenation of New Mexico coal at short residence time and high temperature. Sam Friedman, Raymond W. Hiteshue, and Martin D. Schlesinger (U. S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 6470, 28 pp. (1964). The study was made in a bench-scale, semicontinuous unit at pressures of 500 to 6000 $lb./in.^2$ gage (p.s.i.g.), 480 to 1000°, and residence times of $<$ 1 min. to 15 min. Ammonium heptamolybdate was impregnated on the coal to furnish 1% Mo, based on moisture- and ash-free (m.a.f.) coal. Coal could be rapidly hydrogenated at elevated temps. and pressures to yield large amts. of gaseous hydrocarbons and small amts. of low-boiling oils, high in single-ring aromatics. At 800° and 6000 p.s.i.g. and a residence time of 1 min., the yield of hydrocarbon gas was 43% and of liquid hydrocarbons 9%, based on m.a.f. coal. With a 15-min. residence time, the yield of gaseous hydrocarbons increased to 63% with a decrease in yield of oil to 6%. At higher hydrogen velocities, the yields of oil were much greater but contained large quantities of asphaltene. Low concns. of Mo (0.01 and 0.1%) or a high concn. of Fe (1%) were ineffective at 800°, 6000 p.s.i.g., and short residence time.

5.43 Hydrogenolysis and structure of Hokkaido coals. I. Hiroshi Nagai and Akira Akama (Prefect. Chem. Ind. Res. Inst., Hokkaido, Japan). *Kogyo Kagaku Zasshi* 67(8), 1260-6 (1964). To coal-oil pastes prepd. from 15 Hokkaido coals of different geological age (contg. 60-85% C) and creosote oil, was added 0.3% S and Bayer catalyst, and the pastes were hydrogenated in a 5.5-l. rotating stainless steel autoclave at an initial H pressure of 100 atm., temps. of 425° and 450°, and contact time of 2 hrs. Degrees of coal decompn., degrees of liquefaction, H consumption, light oil yields, and components of the light oil were detd., and the structure of the coals was estd. on the basis of these results. II. Ibid., 1266-70. The structure of Hokkaido coals was estd. from the results of hydrogenation expts. carried out under the same conditions except that the contact time was 0, 0.5, and 1 hr., resp.

1963

5.44 Liquefaction of coal. G. Arich and A. Cocco (Univ. Trieste, Italy). Univ. Studi Trieste, Fac. Ing., Ist. Chim. Appl. No. 12, 84 pp. (1963). Desirable characteristics of coal suitable for hydrogenation include a low content of minerals and moisture and a C:H ratio < 15. A min. of 35% volatile matter and a relatively high % of O and org. S are also desirable. Metal catalysts for coal hydrogenation must be resistant to S. Metalic sulfides possessing catalytic activity should be used. Finely dispersed Ni and Mo are good catalysts but are not superior to Sn. Lignite, however, can be hydrogenated by using 6-7% Fe oxides as catalysts. Coal hydrogenation yields gas, gasoline (b. 40-180°), medium oil (b. 180-330°), heavy oil (b. $>$ 330°), asphalts (C_6H_6-sol.), and insol. residue. The gas fraction consists of CH_4, C_3H_8, C_2H_6, Me_3CH, and C_4H_{10}, in addn. to N, NH_3, H_2S, CO, CO_2, and H_2O. The gasoline fraction contains S, N, and O compds. (alcs., aldehydes, and ketones). Medium oil contains phenanthrene, carbazole, pyrene, methyl- and dimethylpyrene, coronene, and benzoperylene. The oil fractions also contain about 50% of the N and 20% of the S and O originally present in the coal. Other compds. present are phenol, cresols, xylenols, and higher homologs. 125 references.

1962

5.45 Relative activity of impregnated and mixed molybdenum catalysts for coal hydrogenation. M. D. Schlesinger, L. V. Frank, and R. W. Hiteshue (U. S. Bur. Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 6021, 12 pp. (1962). Exptl. data are given to show that when a vehicle oil produced from coal is present, coal is hydrogenated to the same high conversion whether Mo catalyst is impregnated on the coal or intimately mixed with the slurry. Differences in product distribution could be related to the severity of operating conditions. A mixing time of 2 hrs. was sufficient. Hydrogenation conditions were 8500 to 10,000 lb./sq. in. at 400-500° with Mo concns. of 0.01%, 0.1%, and 1%. With 15-60 min. at temp., coal conversions higher than 98% were obtained.

5.46 Liquid-phase hydrogenation of Miike coal in an experimental flow plant. Experimental results with creosote as the vehicle. Tsutomu Sakabe, Yoshiaki Ogoa, Rokuro Sassa, Morio Suzuki, Michio Norie, Yoshio Kambayashi, Tomisaburo Ohisa, Masao Takahashi, and Mitsugu Funaki (Resources Res. Inst., Kawaguchi). Kogyo Kagaku Zasshi 5, 297-303 (1962). By using the continuous unit for liquid-phase coal hydrogenation (ibid. 63, 545 [1960]), the variation in compn. of the products during long runs was investigated. Work was carried out chiefly with creosote as the vehicle. Optimum conditions for hydrogenation of Miike coal with Bayer-mass catalyst were 300 atm., 440° (1st converter) and 460° (2nd converter), 6 kg./hr. of paste, 5.5 normal cu. m./hr. of H, and a rate of gas circulation of 24-32 l./hr. at operating pressure. The following results were achieved: decompn. of coal, 97.2%; asphalt production, 3.0%; light oil b. $<$ 300°, 71.9%; gaseous products, 22.1%.

5.47 Production of chemicals from the anthracene fraction of coal tars by high-temperature hydrogenation. A. G. Borts, A. A. Krichko, R. A. Konyashina, A. V. Lozovoi, and L. N. L'vova. Tr. Inst. Goryuch. Iskop., Akad. Nauk SSSR 17, 250-61 (1962). Hydrogenation of the anthracene fraction for the production of solvents, C_6-C_8 aromatic hydrocarbons, phthalates, and other products was carried out under 100-200 atm. at 520-50°, with a space velocity of 0.5-1.2 kg./l./hr. with a H feed of 2000 l./kg., over MoO_3-Al_2O_3 and CoO-MoO_3-Al_2O_3 catalysts, to obtain yields. of $<$80%.

1961

5.48 Hydrogenation of coal. Wilburn C. Schroeder, Lawrence G. Stevenson, and Thomas G. Stephenson (to Fossil Fuels, Inc.). U.S. 3,152,068 (Cl. 208-11), Oct. 6, 1964, Appl. April 21, 1961; 8 pp. Dry coal, pulverized to 70% through 200 mesh and catalyzed with an $(NH_4)_2MoO_4$ soln. or with a soln. of any other catalyst, followed by drying, is hydrogenated with excess H to tar, liquids, and gaseous hydrocarbons without addn. of a pasting oil under 500-4000 lb./in.^{2} gage and 450-600° for a residence time of $<$ 1 min. With increasing temp. the production of tar and liquid hydrocarbons decreases while that of gaseous hydrocarbons increases. Substantially complete conversion of coal to liquids and gases is obtained with shorter residence time as the temp. is increased. The most favorable temp. for the production of a high proportion of liquids and tars is between 475 and 525°, while for the production of gaseous hydrocarbons a temp. between 650 and 700° is most suitable. Pressures as low as 500 lb./in.^{2} gage provide almost as good conversion to light liquids as pressures at 6000 lb./in.^{2} gage. The max. conversion appears to be obtained at 1500-3000 lb./in.^{2} gage. At 2000 lb./in.^{2} gage and 500°, max. conversion was obtained at approx. 22 sec. when about 30% liquids, 40% tar, and 30% gas was produced.

5.49 Hydrogenation of coal at short retention times. Paul S. Lewis, Henry H. Ginsberg, and Raymond W. Hiteshue (U. S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 5908, 14pp. (1961).---Bench-scale expts. showed the gross effect of retention times ranging from 0.1 to 14.5 min. on the conversion of high-volatile C bituminous coal to liquids and gases. The uncatalyzed coal was hydrogenated at

400, 450, and 538° and at 500, 1000, and 2000 lb./sq. in gage. The % coal conversion increased rapidly during the initial 3 min. and asymptotically approached a max. within 7 min. under all conditions. Reasonably good correlations of coal conversion with time, pressure, and temp. were obtained. Temps up to 900° and retention times of about 1 min. are recommended for future expts. with the objective of producing only gaseous hydrocarbons and partially devolatilized coal suitable for use as a solid fuel. The reactor contained 13 semicircular ledges and the retention time was controlled by the rotation of scrapers which swept the coal from ledge to ledge. Only coal feeds that did not adhere to the internal mechanism could be used.

1960

5.50 Experimental plant for continuous liquid-phase coal hydrogenation. Tsutomu Sakabe, Yoshiaki Ogo, Yoshio Kambayashi, Rokuro Sassa, Morio Suzuki, Michio Horie, Tomisaburo Ohisa, and Mitsugu Hunaki (Resources Res. Inst., Saitama). Kogyo Kagaku Zasshi 63, 545-55 (1960). A 50 kg./day pilot plant for continuous coal hydrogenation at 700 atm. and 450-80° is described. In this plant, preliminary expts. under 200 atm. pressure with Miike Miyanoura coal and Sn oxalate catalysts have been carried out successfully during the past 2 years.

1959

5.51 Investigations on agglomeration during low-pressure hydrogenation of coal in a fluidized bed. Walter Kawa, Raymond W. Hiteshue, William A. Budd, Sam Friedman, and Robert B. Anderson. U. S. Bur. Mines, Bull. No. 579, 1-11 (1959). Agglomeration is the main difficulty during the low-pressure hydrogenation of dry, bituminous coal in a fluidized bed. Expts. with fairly small amts. in a semicontinuous plant have shown that agglomeration can be prevented if the operation is carried out at a relatively low temp. and if the coal is pretreated with an alkali carbonate or $(NH_4)_2MoO_4$ in the presence or absence of H. A diln. of the material with charcoal is also favorable. The residence time at 400-500° must be sufficiently long to get a good yield of oil. There were no agglomeration difficulties during the processing of Texas lignites. From C.Z. 1960, 6020.

1958

5.52 Catalytic decomposition-extraction of coal. Nakaji Yuki and Yoshio Kawana (to Japan Agency of Industrial Science and Technology, Minister of International Trade and Industry). Japan. 6256 ('62), June 28, Appl. Sept. 22, 1958; 3 pp. Pastes made of coal powder and solvent tar were heated at 350-500° with catalysts and carriers to obtain tars having low-boiling components. A powder of Pacific Ocean coal (< 100-mesh) was mixed with a fraction from tar distn. (b. 200-320°) in a 1:3 by vol. ratio to form the paste. CuO (0.5%) was added to the paste, and the mixt. was heat-treated at 400° under a pressure of 20 kg./cm.^{2} for 1 hr. The product was distd. at atm. pressure. The components b. < 300° comprised 75.8% of the product.

C. Physical Parameters of Solvent

1972

5.53 68461n Thermal liquefaction of brown coal in Tyumen petroleum studied by experimental-statistical methods. Bentsianov, Yu. V.; Korolev, Yu. G.; Kuz'micheva, T. A.; Makarov, G. N.; Chuparova, L. D. (USSR). Tr. Mosk. Khim.-Tekhnol. Inst. 1972. No. 70, 238-40 (Russ). The optimal conditions were investigated for prodn. of low-ash coke by liquefaction of brown coal in high-S crude oil fractions b. > 240°. The math. model of liquefaction was based on the effect of parameters, e.g. dissoln. temp., process duration, wt. ratio of solvent and org. mass of coal, and initial moisture of coal on the degree of conversion and yield of ext., gas, and heavy fractions b. > 360°. These equations showed clearly nonlinear characteristics. At < 390°, the degrdn. and dissoln. reactions are predominant, whereas at > 390°, their rates decrease and the secondary decompn. reactions of dissolved coal and reactions of condensation and synthesis are more pronounced. This change is combined with a sharp decrease of heavy fractions in the ext. and their pptn. The dissolving capacity of the solvent depends on the content of polar groups, e.g. S.

1971

5.54 21461x Thermal dissolution of Irsh-Borodinsk brown coal in Arlan petroleum by a fractional factor experiment method. Bentsianov, Yu. V.; Zagorets, A. M.; Korolev, Yu. G.; Makarov, G. N.; Filippovskaya, Z. V.; Chuparova, L. D. (USSR). Sin. Anal. Strukt. Org. Soedin. 1971, No. 3, 215-24 (Russ). From Ref. Zh., Khim. 1972, Abstr. No. 3P113. Soln. was studied of brown coal (moisture content 20-5, ash content 4-5, contents of volatile components, C, and H 46-8, 68.70, and 6.46% resp., and relative to combustible coal mass in Arlan petroleum (b. > 240°, distillate < 300° 9.7, > 450° 58.8% and contg. S 3.12, asphaltenes 9.3, C 84.08, and H 11.18%). Effects of soln. temp. (250-320°), time (10-60 min), solvent:coal ratio, and moisture content of the coal on the extn. yield, ext. compn., and of the parameters were evaluated and regression equations describing these effects were derived.

5.55 18716h Effect of some additives to coals on the properties of the plastic mass they form and on the composition of semicoking products. Tyutyunnikov, Yu. B.; Sintserova, L. G.; Kashirskaya, L. P.; Romodanov, I. S. (USSR). Sb. Nauch. Tr., Ukr. Nauch.-Issled. Uglekhim. Inst. 1971, No. 24, 59-69 (Russ). Coking of coal with the addn. of mazut broadened the liq.-state temp. range for the plastic mass, whereas addn. of paraffin narrowed this range. Mazut decreased the yield of pyrogenic H_2O and increased the yield of phenols, the latter owing to a mazut-caused transformation of the O-contg. substances of coal into phenols. To a gas coal of low degree of metamorphism, org. compds. with a high tendency to split off H and to form inactive free radicals were added, i.e. pyrogallol, pyrocatechol, β-naphthol, and 2,3,5,6-tetramethyl-p-phenylenediamine, in amts. of 0.5-8 wt. %, and the mixt. was rapidly heated to 200, 250, and 300° with a gaseous heating medium. The dynamics of viscosity in the plastic state, Roga index, and concn. of paramagnetic centers were detd. The addn. of 0.5% β-naphthol improved the coking ability and lowered the viscosity in the plastic state the most. Reactions between products of thermal decompn. of coal and H from additives was confirmed by the material balance of the products of semicoking.

1970

5.56 34152c Solvents used in the conversion of coal. Angelovich, J. M.; Pastor, G. R.; Silver, H. F. (Univ. of Wyoming, Laramie, Wyo.). Ind. Eng. Chem., Process Des. Develop. 1970, 9(1) 106-9 (Eng). The results of an exptl. study of the effectiveness of solvents in the liq.-phase catalytic hydrogenation of a subbituminous Wyoming coal in a batch reactor were correlated by using Prausnitz's concept of a nonpolar soly. parameter. Kiebler's exptl. data from a solvent-extn. study of a Pittsburgh seam coal have also been correlated by using this parameter. Solvents with a nonpolar soly. parameter of ~9.5 appeared to be most effective in both studies. Anal. of data from Australian coal-extn. studies and Japanese coal-swelling studies showed similar results. This suggests that the nonpolar soly. parameter may be useful as an addnl. tool for screening solvents proposed for coal liquefaction or extn. processes.

5.57 89545e Solvent effect of vehicle oil in coal hydrogenolysis reaction under high pressure. Maekawa, Yousuke; Shimokawa, Katsuyoshi; Ishii, Tadao; Gan, Takeya (Gov. Ind. Dev. Lab., Hokkaido, Japan). Kogyo Kagaku Zasshi 1970, 73(11) 2347-51 (Japan). A coal hydrogenolysis reaction under pressure was carried out using a shaking-type autoclave. The quality and type of vehicle oil were changed under a given reaction condition to det. the degree of conversion. In the process of the reaction, an intimate relation existed between the degree of conversion and the fluidity of reactants within the autoclave. Under reaction conditions in which the reaction rate was not influenced by stirring, the measured reaction const. showed identical values irrespective of the presence or absence of the vehicle oil and (or) the type of oil. The phenomenon in which the reaction rate varies with the type of vehicle oil was considered hitherto as the solvent effect in the hydrogenation reaction. This actually arises from the effect of vehicle oil on heat and mass transfer process in the reaction. When a complex heterogeneous reaction, such as coal hydrogenolysis reaction under pressure, is carried out using a batch-type autoclave, there are cases in which a proportionate relation does not necessarily exist between the conversion and chem. reactivity.

1967

5.58 5268u Kinetic study of the thermal dissolution of high-volatile bituminous coal. Wiser, Wendell H.; Hill, George Richard (Univ. of Utah, Salt Lake City, Utah). Symp. Sci. Technol. Coal 1967, 162-7 (Eng). Mines Br., Dep. Energy, Mines Resour.: Ottawa, Can. Dissoln. was done in Tetralin at 350-450°. The fraction extd. after 6 hrs. at 400° became max. and const. when 8 ml. Tetralin/g. coal was used. Initial reactions were 2nd order with enthalpy of activation 28.8 kcal./mole. The latter parts of the reactions were 1st order with enthalpies of activation 15.6 kcal./mole.

1965

5.59 Use of surface-active agents in the extraction of solid fuels. Lidia Wnekowska, Amalia Tobiczyk, Barbara Wojciechowska, and Barbara Wojakowska. Prace Glownego Inst. Gornictwa Komun. No. 378-386, 367-73 (1965) (Pol). Tests on several different solid fuels showed that surface-active agents increase the yield of substances extd. by acetone and by Tetralin. Tetralin was a better solvent than acetone. Nonionic surfactants had the greatest effect. However, no regularity of variation in the yield of ext. could be established, either related to the type of fuel or to the type of wetting agent.

1963

5.60 Agitation in liquid-phase coal hydrogenation and its scale effect. Tsutomu Sakabe and Yoshiaki Ogo (Resources Res. Inst., Kawaguchi, Japan). Kogyo Kagaku Zasshi 66(12), 1875-80 (1963). A study of agitation in a liquid-phase hydrogenation reactor showed that the agitation was sufficient at standard reaction conditions of 300 atm., 445-465°, a coal-paste feed rate of 0.6-0.7 kg./l.hr., and a H:coal paste ratio of 2-2.4 m.^{3}/kg. The effects of thermal expansion, absorption, and consumption of H by a liquid were examd. by using an aq. 0.5N Na_2CO_3 soln. instead of the coal paste, and 4 similar reactors of different sizes were used to study the scale effect. The agitation did not depend on the H:coal paste ratio, but the linear velocity of H gas charging must be proportional to the diam. of the reactor to achieve a corresponding agitation effect. This can be explained by dividing the agitation effect into 2 factors, one dominant in the mixing of liquids, and the other dominant in suspending solid particles, such as a catalyst, in the liquid.

1962

5.61 Solvent extraction of coal. Yuzo Sanada and Hidemasa Honda (Resources Res. Inst., Saitama-Ken). Bull. Chem. Soc. Japan 35, 1358-60 (1962). The customary method of Soxhlet extn. was modified by using solvents at their b.p. to preclude the rejection of several solvents by earlier investigators on the suspicion of chem. effects, poor dissolving power, or incompleteness of extn. The cohesive energy d. for 14 solvents, e_{gs} (cal./cc.), was calcd. from the following relation: $e_{gs} = (L_b - \mu RT)V_b$ where L_b is the latent heat of vaporization at the b.p. in cal./mole, V_b is the mol. vol. at a normal b.p. in cc./mole, R is the gas const., T is the b. temp. in °K., and μ is the correction term in $\mu = PV/RT$. (For substances b. $>50°$ the μ correction can be neglected.) V_b was calcd. by the additive method by using LeBas's vol. increments (cf. Rein and Sherwood, Properties of Gases and Liquids, 1958, p. 51). The av. error of the compd. tested was 4.7%. The value of L_b was available in the literature. The yield of ext. at the b.p. together with certain phys. data are shown for the 14 solvents used with b.ps. from 61° to 202°.

5.62 Effect of pressure during thermal decomposition of coal. M. G. Sklyar and V. I. Shustikov. Khim. i Tekhnol. Topliv i Masel 7, No. 8, 39-42 (1962). In the thermal processing of solid fuels, external pressure exerts a marked effect in promoting internal reactions within the particles, in lowering the av. mol. wt. of the org. mass, in raising the soly. of the products in org. solvents, and in increasing the plasticity at a given temp. A coal heated to 390-400° in a lab. autoclave from which the air had been purged with a fuel gas had, under 1 kg./sq. cm. pressure, a soly. in C_6H_6 of 25.05%, and, under 49 kg./sq. cm., 32.68%. At pressures of 1.0, 49.2, and 92.5 kg./sq. cm., gas yields from 1 kg. of coal were 30.0, 15.0, and 3.61., resp.; H yields, —, 1.36, and nil.

1961

5.63 Hydrogenolysis of coal. Hisashi Hara, Hirohisa Kudo, and Kiyoshi Mizushima. Nenryo Kyokaishi 40(411), 545-55 (1961). The speed of hydrogenolysis of coal depends upon the speed of soln. of H in the liquid phase and on the no. of collisions between H and coal particles. The influence of preliminary heat treatment of the paste on hydrogenolysis, size, and sedimentation rate of the coal particles in the paste, as well as the viscosity of the paste, was studied. The soly. of H in the paste and the paste oil was detd. The paste is better suited for the hydrogenolysis, which should be carried out at the highest possible pressure and temp. From CZ 1963 (49), 21764.

D. Treatment of Coal Products

1973

5.64 5620p Hydrocracking of distillates of coal origin. Krichko, A. A.; Yulin, M. K.; Ravikovich, T. M.; Skvortsov, D. V.; Muselevich, D. L.; Zamanova, L. P. (Inst. Goryuch. Tskop., Moscow, USSR). Khim. Tverd. Topl. 1973, (4), 75-81 (Russ). Results of hydrocracking of the hydrorefined distillate (b.p. $>$320°) of a vacuum gas oil from the Romashkino petroleum and of the hydrorefined distillate (b.p. 180-320°) from the liq. coal hydrogenation products on zeolite catalyst were given. At 380° and 40 atm, hydrocracking of gas oil fraction gave conversion of 31.3-34.5%, whereas that of the liq. coal hydrogenation products gave 52.6% gasoline of b.p. $<$ 180° and 9% gas per 1 passage. The zeolite catalyst activity did not change after 800 hr.

1972

5.65 5624t Quality of synthetic gasoline from coal. Qader, S. A.; Singh, Surjit; Hill, G. R. (Dep. Min., Metall. Fuels Eng., Univ. Utah, Salt Lake City, Utah). Amer. Chem. Soc. Div. Fuel Chem., Prepr. 1972, 16(1), 36-43 (Eng). The quality of coal gasoline depends mainly upon the nature of the coal oil and the processing conditions. The nature of the coal oil in turn depends upon the coal conversion process. The coal gasolines prepd. from different coal oils by hydrotreatment were high in arom. content (65-85%). The arom. content of the coal gasoline was reduced to 30% by extn. by DMF. The arom. extract was hydrodealkylated under mild conditions to produce benzene-toluene-xylene fraction (BTX). The effect of producing low arom. gasolines and BTX from coal oil on the economics of the coal hydrogenation process was discussed.

5.66 142174y Pressure influence on yield of coal extraction. Rauk, Jerzy; Rutkowski, Alojzy; Rutkowski, Marian (Nauk. Inst. Chem. Technol., Politech. Wroclaw., Wroclaw, Pol.). *Pr. Nauk. Inst. Chem. Technol. Nafty Wegla Politech. Wroclaw*, 1972, 11, 43-53(Pol). The effect was detd. of pressure on the extn. of low-carbonization coal with raw and hydrogenated anthracene oil. In the presence of 6.8% H in the solvent, the free-radical character of the chem. reactions and the yield of extd. products were independent of the pressure at 30-120 atm, the yield was ∼55%. With 5.4% H in the solvent at higher pressures the kinetic characteristics of the extn. process changed considerably and the yield of extd. products increased (yields were 25 at 36 and 39% at 120 atm).

1971

5.67 138405y Conversion of coal by solvent extraction. Gorin, Everett (Consolidation Coal Co.) U.S. 3,748,254 (Cl. 208-8, C 10g), 24 Jul 1973, Appl. 205,788, 08 Dec 1971; 6 pp. High-S coal is converted by solvent extn. at an elevated temp. to a mixt. of ext., solvent, and undissolved carbonaceous residue. The mixt. is sepd. into a low- and high-solids fraction. The low-solids product is useful as a fuel or as an intermediate in the production of low-S liq. fuels by hydrogenation. The compn. of the high-solids product is adjusted to provide a fluid compn. such that the relative proportions of solids, solvent, and ext. will give a pelletizable product consisting essentially of solids and a liq. binder consisting of the solvent and the ext. Pellets are preferably formed in a rotary drum and hardened either concurrently with or immediately after formation. The hardened pellets can be used as solid fuel or as an intermediate in the prodn. of gaseous and liq. fuels by C-steam reactions.

5.68 21488m Integrated coal liquefaction and hydrotreating process. Correa, Juan Jose; Hochman, Jack Martin (Esso Research and Engineering Co.) S. African 72 00,812 (Cl. C 01g), 08 Sep 1972, US Appl. 116,373, 18 Feb 1971; 24 pp. Coal liquefaction and coal liq. hydrotreating zones are operated at essentially equiv. temps. and pressures. One portion of the liq. product from the liquefaction reactor is heated by means of the vapor product from the liquefaction reactor for feed to a hydrotreating zone. The other portion of the liq. product is fed the hydrotreating zone for quenching.

1966

5.69 Processing of coal tar by hydrocracking at low pressure. Ya. R. Katsobashvili and E. I. El'berg. Koks i Khim. 1966(1), 43-7 (Russ); cf. CA 63, 6350f. Methods of coal tar processing and previous work by the author are reviewed. New exptl. data on hydrocracking at 500-50° and 50 atm. with an Al-Co-Mo catalyst and C_6H_6 as diluent are tabulated and discussed. A tech. scheme of a corresponding plant for complex tar processing is given. Yields of the com. products by the present and proposed methods are tabulated. The total yields of com. products were 36.9 and 83.8% resp. and the yield of aromatic hydrocarbons was increased.

5.70 Coal uses off the beaten path. J. F. Cudmore (Australian Coal Ind. Res. Labs. Ltd., Chatswood). Australian Chem. Process Eng. 19(3), 16-22 (1966) (Eng). Two potential new uses for Australian coals are described: the production of a nitrogenous fertilizer and a de-ashed coal by solvent extn. At the Central Fuel Research Institute of India (CFRI), N-enriched coal is prepd. in a 7-in. fluidized-bed reactor system by reaction of powd. coal in a fluidized bed with a stream of an air/NH_3 mixt. at 300° for a few hrs. A process for de-ashing of coal by solvent extn. has been developed by the Spencer Chemical Division, Gulf Oil Corporation, U.S.A. Coal and a high-temp. "cut" of anthracene oil are mixed together in slurry tanks at ratios of solvent to coal varying from 2:1 to 4:1. H is added to the slurry just before preheaters, which heat the mixt. to maintain a temp. of about 460° in the dissolver tubs for given times and pressures. After treatment, the pressure is released, the H largely recovered, and the coal soln. filtered through a rotary pressure precoat filter. The dissolved material from the filter is vacuum flash evapd., the solvent removed for recycle, and the product (liquid at this stage) pumped onto a water-cooled continuous steel belt, where it solidifies. Solvent is produced in the reaction. The mechanism of solvent extn. was considered to be based on initial thermal depolymerization of the large coal mol. The H acts as a terminator of free radicals, which cause repolymerization and make filtration difficult in case of delays. The low-ash coal resembles a hard coal tar pitch. In one case, ash content was reduced from 7.13 to 0.48%, with another coal from 4.20 to 0.17%. With the redn. in ash, there is a significant increase in the heating value of the products. Possibilities for its use as a gas-turbine fuel, blending with diesel oil for railroad fuels, and C electrodes for Al refining are reviewed.

1965

5.71 Chemical structure and properties of coal. XXVIII. Coal constitution and solvent extraction. D. W. van Krevelen. Fuel 44(4), 229-42 (1965) (Eng); cf. CA 54, 23260g. Two important questions with regard to the solubility of coal in org. solvents are: (a) Why does the potentially sol. fraction of coal decrease with increasing coalification, approaching 0 at a 92% C content? (b) Why has every solvent its optimum extg. effect at a specific coalification degree? The first question is answered by Flory's theory of trifunctional stepwise polycondensation. In accordance with exptl. facts, this theory predicts that exts. of cross-linked polycondensation products always contain a considerable fraction of low-mol.-wt. material. The magnitude of the structural units in coal can be derived from extn. measurements. The 2nd question is answered by calcg. the so-called solv. parameter of coal. The extn. max. for pyridine must lie at a C content of about 88.5%.

5.72 Pressure hydrogenation of tar distillates. Oldrich Svajgl. Sb. Praci Vyskumu Chem. Vyuziti Uhli, Dehtu Ropy 5, 89-106 (1965) (Czech). Conditions for the selective hydrogenation of N bases in brown coal tar distillates were investigated for the purpose of minimizing the loss of aromatic hydrocarbons through hydrogenation. At 320 atm., the selectivity of the hydrogenation can be improved 3-4 fold by raising the temp. to 420° from 360°, and simultaneously increasing the charge rate. Another effective step for decreasing the hydrogenation of aromatic hydrocarbons from 70-80% to 10-20% is to replace the W-Ni catalyst with a Mo-Ni or esp. a Mo-Co catalyst on alumina. Reducing the concn. of W in the W-Ni catalyst to 10% results in lower hydrogenation of aromatics while eliminating N bases to <5 mg. NH_3/l. The selectivity of the process rises rapidly with a lowering of the hydrogenation pressure. Only with the W-Ni catalyst at 420° and 100 atm. is it possible to reduce the content of N bases in the tar distillate to acceptable limits. The phenols b. $\leq 320°$ in the tar distillate are hydrogenated to cyclic alcohols, instead of aromatic hydrocarbons, and ultimately to monocyclic naphthenes. The duration of the working cycle of the catalyst under these conditions is ~1000 hrs. at a charge rate of 0.7 kg. feedstock/l. catalyst/hr., and the resulting fraction, b. $>150°$, is hydrocracked with difficulty and has a low cetane no. The diln. of tar distillates with motor fuel from a petroleum crude permits the blend to be hydrogenated at 100 atm. and up to 400° at a charge rate of 1.25 kg./l. catalyst/hr. This yields a high-quality grade of aromatic gasoline with a high concn. of low-boiling aromatic hydrocarbons and a paraffinic motor fuel of cetane no. 45 and

0.02-0.05 S. It is necessary, however, to avoid carefully mixts. which ppt. insol. resins. Such resins result from the pptn. of pyrocatechols from the tar and of paraffin wax from the petroleum crude, which are insol. in the mixt., and may be described as asphaltic material derived from tar. The resins are formed 24-28 hrs. after mixing in the ratio of 1 part tar distillate to 2 parts petroleum crude distillate. If the tar distillate is freed of pyrocatechols by hydrogenation, resins do not ppt. even after 1 month standing. Under the hydrogenation conditions, the blended petroleum motor fuel is desulfurized to 95%, which is 15% better than required when it is refined in the unblended state. Since the reaction temp., pressure and charge rate are limited by the hydrogenation of the N bases, it is possible to add to the appropriate product a certain amt. of non-hydrogenated petroleum motor fuel. This compensates in part for the ultimately higher consumption of H in overhydrogenation of the motor fuel in the blended feedstock, and in part for the requirement of a larger reaction chamber. The test app. provided a reaction space of 200 ml. packed with catalyst of 1-2 mm. grain size. The feedstock was sprayed into the stream of hydrogenation gas (70-80% H, balance predominantly N and CH_4) and was indirectly heated elec. in the upper part of the reactor, which was packed with stainless-steel rods. The ratio of gas to feedstock was 2000:1 for the tar distillate and 500:1 for the blended feedstock. The catalyst at the start of the expts. was held 24 hrs. in a stream of hydrogenating gas contg. 1-2 g. $H_2S/m.^3$ to convert the oxides of the active metals to sulfides.

5.73 Hydrocracking of low-temperature tars. Marian Rutkowski (Politech. Wroclaw, Poland). *Zessyly Nauk. Politech. Wroclaw., Chem.* No. 12, 3-28(1965) (Pol). Raw materials, app., and procedure are described for periodic hydrocracking of low-temp. tars from bituminous coal at 430-500° and 70-225 atm. The raw materials were heavy oil from the low-temp. process and its 49:43:8 mixt. with the medium oil and gasoline. The heavy oil had d_{20} 1.097, viscosity at 100° 4.0° Engler, and ignition temp. 185°, and contained ash 0.12, total S 0.74, coke 10.1, asphalts and resins 29.5, matter insol. in C_6H_6 1.11, and H_2O 0.4%. It distd. as follows: beginning at 208°, 10% at 219°, 20% at 331°, 40% at 352°, and 65% (end of distn.) at 366°. Increase of temp. of hydrocracking increased the yield of gasoline, coke, and gaseous products, decreased the yield of residues remaining after distn. to 325° and the amt. of asphalts and resin pptd. from this residue by gasoline. An increase in pressure decreased the yield of coke and gaseous products and increased the degree of cracking and hydrogenation of asphalts and resinous products. An increased ratio of H to raw material inhibited the coking process and increased the yield of gasoline and gaseous products. Expts. with and without several types of contact catalysts showed that, in the absence of catalysts, unstable, easily polymerizing products were formed. Fe oxides increased the activity of some catalysts employed. Among diluents such as Tetralin (I), cyclohexane (II), crude and pure C_6H_6, and synthetic and low-temp. gasolines, I and II had the greatest influence on decrease of coke yield.

5.74 Vapor-phase hydrogenation of oils derived from coal and oil shale. C. O. Hawk, M. D. Schlesinger, H. H. Ginsberg, and R. W. Hiteshue (U. S. Bur. of Mines, Pittsburgh, Pa.). U. S., Bur. Mines, Rept. Invest. No. 6548(1), 53 pp. (1965) (Eng). Single-step, catalytic, vapor-phase hydrogenation of oils derived from coal and oil shale was studied. Treatment of middle oil from hydrogenation of bituminous coal gave good yields of gasoline with a German Mo-Zn-Cr catalyst. Good results were also obtained with duplicates of this catalyst made from domestic raw materials. In 1 set of expts. with the German catalyst, 38-52 wt.% of the feed was converted to gasoline. The total liquid product was 91-8 wt. % of the feed. Not all this gasoline can be claimed as production because ~20% of the feed was in the gasoline range and part of it undoubtedly survived the hydrocracking treatment. Hydrogenation of crude shale oil in the presence of a Co molybdate catalyst produced a total liquid product of 89 wt. % of feed. The hydrogenation converted 27 wt. % of the feed to gasoline and 44 wt. % to diesel fuel. The remaining liquid product, 18 wt. % of feed, was residue boiling above diesel fuel. The gasoline was of poor quality, octane no. 39.1. The overall product seemed to be a suitable feed stock for conventional refining. Coker distillate hydrogenation by using a Co molybdate catalyst gave a total liquid product of 97 vol. % of feed, of this product, 60 vol. % was jet fuel and 40 vol. % was diesel fuel. High N and S in all 3 of these raw materials severely poison the usual refining catalysts. The common objective in these studies was use of poison-resistant catalysts in order to reduce N and S to tolerable levels. Co molybdate was an esp. effective catalyst for S removal.

5.75 Reaction kinetics of coal hydrogenation under high pressure. Tadao Ishii, Yousuke Maekawa, and Gen Takeda (Univ. Hokkaido, Sapporo, Japan). Kagaku Kogaku 29(12), 988-95 (1965) (Japan). Previous kinetic data show that asphaltene is an intermediate product in the overall hydrogenation of coal into distillable oil. However, very little kinetic data on hydrogenation of Japanese coal and asphaltene have been published. To obtain numerical values of reaction rate covering a wide range of reaction conditions that might possibly occur in the reactor and to re-examine the reaction mechanism, a batch autoclave study was made on the kinetics of the hydrogenation of 2 Japanese coals and 1 Japanese asphaltene. The coal hydrogenation consists of 2 steps. The rate of reaction in the 1st step is high and that in the 2nd step is much slower. Both steps can be expressed as a 1st-order reaction with respect to the coal remaining. The hydrogenation reaction of asphaltene consists of 1 step, which may be expressed as a 1st-order reaction. The reaction of Hokkaido brown coal is represented schematically.

1964

5.76 The Houdry Litol Process. Alexander K. Logwinuk, Lee Friedman, and Alwin H. Weiss (Houdry Process and Chem. Co., Philadelphia, Pa.). Erdoel Kohle 17(7), 532-7 (1964) (Eng). A process is described which allows the production of high-quality aromatics (C_6H_6, PhMe, xylene) from coke-oven light oils. The products are competitive with petroleum-derived aromatics. The feed is vaporized, mixed with H, passed through a preliminary catalyst bed to sat. styrenes, heated, and passed through the main catalyst bed. There the following reactions occur: (1) hydrogenation of S compds., primarily thiophene, to satd. hydrocarbons and H_2S; (2) catalytic hydrocracking of satd. hydrocarbons to lower-mol.-wt. satd. hydrocarbons which can be sepd. by fractionation; (3) dehydrogenation of cyclic olefins to aromatics; (4) hydrogenation of olefins to paraffins. Side reactions are minimized. Catalyst modification or adjustment of operating conditions permit a hydrodealkylation of C_6H_6 homologs if desired. C_6H_6 of the following specifications can be produced: f.p. $>5.4°$; thiophene content <0.5 p.p.m.; acid wash color $<$o+.

1963

5.77 Destructive and nondestructive hydrogenation of tars. Badische Anilin- and Soda-Fabrik A.-G. (by Hanns C. Wille). Fr. 1,401,376 (Cl. C 10g), June 4, 1965, Ger. Appl. April 20, 1963, 3 pp. To impart a long catalyst life, fresh H must be used for destructive hydrogenation. For economical working, this recycle H is used, without decompression, for nondestructive hydrogenation, supplemented, if necessary, by fresh H. Thus, a mixt. of lignite tar (40% b.p. 325°), 460 m.^{3}/hr. refined tar, and 20,000 m.^{3}H/hr. at 300 atm. was heat exchanged with outflowing material to 200°, then gas heated to 300°, and passed through a bed of 25% Co molybdate and 3% NiS on an active Al_2O_3 catalyst, the temp. rising to 325°. After cooling by heat exchange with the inflowing mixt. and a condenser, the gas was recycled and the liquid distd. at atm. pressure to give a liquid b. 360° and a residue. The liquid was deparaffinated with liquid C_3H_8 and EtOAc, then vacuum distd. to give a light or spindle oil and a lubricating oil.

The latter oil was mixed with 480 m. /hr. fresh H and 10,000 m.^{3}/hr. recycle H heated as before by heat exchange and gas to 330°, and passed through 3% W-Ni-S on active Al_2O_3, cooled by heat exchange and gas in excess of $>$10,000 m.^{3}gas/hr., and 460 m.^{3}/hr. refined tar was recycled to the 1st stage.

5.78 Catalytic hydrogenation of coal-tar components by molybdenum sulfide. Shinji Shono and Midori Yamada (Nippon Univ., Tokyo). Koru Taru 15(9), 405-10 (1963). The authors' recent studies in catalytic hydrogenation of hydrocarbons (C_6H_6, PhMe, o-xylene, pseudocumene, PhEt, cyclohexane, methylcyclohexane, m-dimethylcyclohexane, biphenyl, naphthalene, acenaphthene, anthracene, cyclohexene, and phenanthrene), O compds. (phenol, o-, m-, and p-cresol, 1,3,5-xylenol, α-naphthol, and β-naphthol), N compds. (pyridine, 2,4-lutidine, quinoline, carbazole, piperidine, aniline, α-naphthylamine, benzonitrile, and α-naphthonitrile), S compds. (benzothiophene, thiophenol, thiophene, and thionaphthene), and anthracene oils (anthracene cake, anthracene oil, anthracene light oil, and anthracene oil freed from crystals) are reviewed. 41 references.

5.79 Hydrogenation of coal extracts. Everett Gorin (Consolidation Coal Co.). U.S. 3,117,921 (Cl. 208-8), Jan 14, 1964, Appl. Jan 21, 1963; 4 pp. Coal extd. as in U. S. 3,081,241 (CA 58, 12180d) is prehydrogenated at 425-470°, 500-2500 lb./sq. in. and 10-30 min. residence time to partially convert the ext. to a distillate boiling $<$ 325°. The H transfer may be from hydrogenated product oil; free H may be added to aid the hydrogenation. The operation may be noncatalytic or in the presence of 0.05-1.0% by wt. of a H halide or its ammonium salts, e.g. NH_4Cl, NH_4Br, or NH_4I; red mud may also be used. The hydrogenated oil:ext. ratio is 1-3:1, preferably mixed with solvent. The $<$325° material is catalytically hydrogenated at 2000-3500 lb./sq. in. and 410-55° in the presence of W or Mo oxides or sulfides impregnated on a refractory support. The $>$325° material is carbonized at 425-760° to yield a liquid distillate; the lower-boiling portion is subsequently hydrogenated.

1962

5.80 Liquid fuels from coal. Everett Gorin (Consolidation Coal Co.). U.S. 3,162,594 (Cl. 208-57), Dec 22, 1964, Appl. April 9, 1962; 7 pp. A process is described for minimizing the deleterious effect of ash having a diam. $0.01\ \mu$ on a hydrocracking catalyst during the production of distillable liquid hydrocarbons from an ash-contg. coal ext. (I). Thus, I, obtained by solvent extn. of a Pittsburgh seam coal at 380° with Tetralin as solvent, was passed to the hydrogenation zone mixed with crushed, deactivated hydrocracking catalyst (II) that had been previously used for hydrocracking a similar ext. I contained 0.18% ash and 38% C_6H_6-insol. matter. About 50% of the ash was insol. in I and had a particle diam. $>0.01\ \mu$. The remaining ash was sol. in I and had a particle diam. $<0.01\ \mu$. II, when originally passed to the hydrocracking zone, was an Al_2O_3-base catalyst contg. 13% by wt. MoO_3 and 3% by wt. CoO. The catalyst was used until no further absorption of ash occurred (the catalyst had adsorbed 10.5% by wt. ash) and then was regenerated with air to remove C. The regenerated catalyst was crushed to a particle diam. of 0-200 μ. The conditions in the hydrogenation zone were 440°, 3500 psig., H feed rate 15 ft.^{3}/lb. I, residence time 1 hr., and a catalyst:I feed ratio of 0.046. The yields were C_{1-4} 5.6, butanes 1.5, C_5 distillate oil (b. $<400°$) 35.4, and nondistillable liquid hydrogenation product (b. $>400°$) 54.2% by wt. of I feed. The H consumed was 4.0% by wt. of I feed.

5.81 Hydrogenation of pitch from low-temperature carbonization of coal. Richard D. Graves, Walter Kawa, and Raymond W. Hiteshue (U.S. Bur. of Mines, Pittsburgh, Pa.). U.S. Bur. Mines, Rept. Invest. No. 6124, 15 pp. (1962). The pitch was hydrogenated at cracking conditions in a continuous bench-scale unit to det. whether good yields of low-boiling liquid hydrocarbons and tar acids could be obtained. The pitch contained 15.6% C_6H_6-insol. material, 4% hexane-sol. oil, and 80.4% asphaltenes by wt. At 475°, 7500 lb./sq. in., and 1.5 hrs. residence time, hydrogenation products, based on the wt. of pitch, were about 36% oil boiling $<325°$, 24% hexane-sol. heavy oil, 17% asphaltenes, 1% C_6H_6-insol. material, and 12% hydrocarbon gases. The yield of tar acids boiling $<250°$ was 4.3%, and the yields of C_{6-8} paraffins, naphthenes, and aromatics were each $<1.0\%$. The yield of tar acids was within the range of yields obtained by hydrogenation or high-temp. carbonization of bituminous coal (2-5 wt. %). There was little or no effect of residence time on yields of alkali-sol. material which contained tar acids. Yields of hydrocarbon gases increased markedly with increase in temp. from 475° to 500°. Lowering the H pressure to 2400 lb./sq. in. gage gave yields similar to those obtained at 7500 lb./sq. in. gage.

5.82 High-energy fuels derived from coal. Maurice Letort. Chim. Ind. (Paris) 87, 371-87 (1962). Production of fuels from coal for jet airplanes is reviewed, including processes for obtaining polynaphthenic hydrocarbons by hydrogenation of coal-tar fractions with Raney Ni and the use of sulfide catalysts, e.g. MoS_2 on activated C, to enable perhydrogenation and controlled hydrocracking to be effected in a single stage.

5.83 Dealkylation of tar oil in the presence of an alumina catalyst. Effects of pressure and temperature. Sumio Matsuda, Shoichi Kikkawa, and Akira Uchida (Osaka Univ.). Kogyo Kagaku Zasshi 65, 568-74 (1962). By continuous hydrodealkylation of the methylnaphthalene fraction, b. 215-60° and contg. 10.6% naphthalene (I) and 46.4% methylnaphthalene (II), from tar oil on an Al_2O_3 catalyst at 600-50° and 30-50 atm., H, C_6H_6, PhMe, xylene, and I were produced. The effects of pressure, temp., and residence time were investigated. At 30-50 atm., 600-50° and 20-40 sec. were preferred; while at 50 atm., 650° was preferable, with the effect of resistance time negligible. Under optimum conditions (50 atm., 650°, and 33 sec.), liquid products contg. C_6H_6 5.6, PhMe 6.1, I 38.3, and II 8.6% were obtained in a 70.2% yield.

5.84 Two-stage production of chemicals by hydrogenation of tars from Cheremkhovo coals. II. A. V. Lozovoi, D. L. Muselevich, T. M. Ravikovich, T. A. Titova, and V. F. Cherkasova. Pr. Inst. Goryuch. Iskop., Akad. Nauk SSSR 17, 174-81 (1962); cf. CA 55, 25226a. Hydroaromatization on a lab. scale of the partially dephenolated distillate of the liquid hydrogenate from semicoking at 75 atm. and 510° in the presence of a MoO_3-Al_2O_3 catalyst at a vol. rate of feed of 0.70-0.75 kg./hr. gave a high degree of conversion into various chem. products and C_{1-4} paraffins. As a result of the 2-stage hydrogenation and the previous removal of the C_{6-8} phenols and bases, 62-6% aromatic hydrocarbons, naphthalene, solvents, phenols, etc.; 33-7% gaseous paraffins, and 5.7-6.0% tars were obtained.

1961

5.85 Liquid fuels from coal. Everett Gorin (Consolidation Coal Co.). U.S. 3,143,489 (Cl. 208-8), Aug 4, 1964, Appl, Nov 24, 1961; 9 pp. Coal is converted to synthetic liquid fuels which boil < 200° through a series of sequential, partial conversion steps designed to increase the H content or to decrease the C content of the coal. The process comprises (1) coal extn. through a hydrocarbonaceous solvent, such as Decalin, biphenyl, phenol, cresol, or xylene; (2) sepn. with simultaneous hydrogenation of the ext. (80% of the MAF (moisture and ash-free) coal is economic optimum) from undissolved coal residue; (3) primary catalytic hydrocracking to convert a major portion of the nondistillable coal ext. to an ash-free, distillable, hydrocarbonaceous liquid b. 500°. Mild catalytic hydrogenation minimized gas and coke formation; (4) Catalytic hydrofining to remove substantially all of the NOS contaminants from the ash-free, distillable, hydrocarbonaceous liquid fraction, preferably b. ≤400°; and (5) secondary catalytic hydrocracking to lower the b.p. range of at least the higher-boiling fraction of the effluent hydrofining products. Thus, any coal, lignite, bituminous, and subbituminous, may be treated. Preferably, the volatile matter should be at least 20%. The solvent-extn. process may be continuous, batch, countercurrent or staged. The temp. can range from 300° to 500°, the pressure from 1 to 6500 lb./in.^{2} gage, the residence time from 1 to 120 min., the solvent:coal ratio from 0.5:1 to 4.0:1 and, if desired, in the presence of a catalyst and/or up to 50 standard cu.ft. of H/lb. MAF coal. Hydrocracking catalysts comprise a mixt. of a Group VIB oxide or sulfide with a Group VIII metal. Preferably, the catalyst hydrocracking zone is a composite of Al_2O_3, an oxide of Mo, and at least one oxide from the group of Fe and Co. Hydrofining catalysts comprise any of the oxides or sulfides of the transition metals and esp. an oxide or sulfide of a Group VIII metal mixed with an oxide or sulfide or a Group VIB metal (preferably Mo or W). Such catalysts may be used in the undild. form but normally are supported on an adsorbant carrier, such as Al_2O_3, SiO_2, ZrO, TiO_2, and naturally-occurring, porous supports, such as bauxite or bentonite. Preferably the carrier should display relatively little cracking activity, and thus highly acidic carriers are generally to be avoided. The undissolved coal residue is sepd. from the coal ext. through filtration, centrifuging, sedimentation, and hydrocloning. Furthermore, the C_6H_6-insol. rich coal ext. is sepd. from the whole ext. in this step. The remainder of the unconverted coal ext. is recovered from the primary catalytic hydrocracking zone and thereafter coked to yield a liquid distillate and coke.

5.86 Composition of the product from medium-pressure hydrogenation of a coal-tar distillate. R. Vaidyeswaran, S. H. Zaheer (Regional Research Lab., Hyderabad), and H. Pichler. Chem. Age India 12, 105-10 (1961). The refining, hydrogenation of a low-temp. coal-tar distillate, with a fixed bed of a desulfurizing catalyst (Co oxide-Mo oxide supported on Al_2O_3) are considered.

5.87 Composition of commercial liquid-phase hydrogenation mixtures. VIII. Composition of the highly condensed aromatic hydrocarbons. R. I. Sidorov, A. A. Khvostikova, A. S. Nakhmanovich, and N. I. Shergina. Trudy Vost.-Sibir. Filiala, Akad. Nauk SSSR, Ser. Khim. 1961, No. 38, 95-102; cf CA 56, 11884e; 57, 4930f. From liquid-phase hydrogenates of medium-temp. tars from Cheremkhovo coal, 26 kg. of neutral oil was produced which, by rectification, gave a 5-kg. fraction, b. 360-420°. This fraction was chromatographed on silica gel to obtain a 2.5-kg. hydrocarbon concentrate of n^{20}_{D} 1.63-1.66. Fractional distn. through a lab. column of 20 theoretical plates at a 10:1 reflux ratio produced some 50 fractions which were analyzed quant. as to chem. "types" (2A =

2 aromatic fused rings, 2A1N = 2 aromatic fused rings and 1 naphthenic fused ring) present in each. It was established by the n-d-M method (*loc. cit.*) that the predominant type of hydrocarbon in the concentrate was 2A1N (tetrahydroanthracenes, phenanthrenes, and acenaphthenes) followed in order by types 4A (pyrenes), 3A, 2A, and 2A2N. By ultraviolet spectral comparisons, it was shown that the ratio of the amts. of phenanthrene and its homologs to anthracene and its homologs was 4.4:1. Ten pure 4A compds. were isolated by repeated distns. and recystns. of the several fractions b. >380° and identified as the following pyrenes: (substituents, m.p. of the compd., m.p. of its picrate): H, 152°, 230°; 4-Me, 146°, 200°; 1-Me, 110-15°, 199°; 1-Et, 135-8°, 198°; 4,9-di-Me, 235°, 230°; and the following unidentified pyrenes, m.p. 117°, 196°; 125°, 202.5°; 128°, 204°; 122°, and 208°. Chrysene was isolated from the highest boiling fractions.

5.88 Composition of commercial liquid-phase hydrogenation mixtures. IX. Composition of the aromatic hydrocarbons in liquid-phase hydrogenates of medium-temperature tars from Cheremkhovo coal. R. I. Sidorov. *Ibid.* 103-111. From previous data and from addnl. studies, calcns. were made of the "type" compn. of the title hydrocarbons by using the n-d-M method on the wide-range concentrates as well as on their narrow-range fractions after distn. Use of the n-d-M method before distn. gave more accurate results, chiefly by avoidance of distn. losses; its use after distn. afforded a detn. of minor constituents. The fractions b. 50-170° contained only benzene and its homologs. Indams appeared in the range 170-202° and Tetraline at 202-60°. Naphthalene homologs were present in minor amts. above 280°. Above 280°, the 2A1N type appeared. The fraction b. 320-400° was sepd. into 3 concentrates by chromatography on silica gel which were then fractionally distd. Type 1A1N appeared largely in the first (lowest silica gel affinity) concentrate fractions b. to 385°; type 1A2N b. to 385°; above this point type 2A2N appeared. Type 2A occurred only in small amts. in the 2nd and 3rd concentrates. Type 2A1N was predominant in all 3 concentrates (49% in the 1st). Most of type 3A appeared in the 2nd concentrate and of type 3A1N in the 3rd. Type 4A was found in the crystn. ppts. of the high-boiling fractions and was confirmed by ultraviolet spectra. Above 400°, 3A1N was the predominant type but 3A, 4A, and 4A1N and 4A2N were present in minor amts. Types were also estd. in 3 new hydrogenates--two from coal tar and one from coal--and the results were in good agreement with the above.

1960

5.89 Reduction of polyhydric phenols with carbon. T. A. Antonova and V. E. Rakovskii. *Tr. Kalininsk. Torf. Inst.* 1960, No. 11, 29-39. A description is given of the partial redn. of polyhydric phenols (e.g. catechol) with activated coal at 440-60° to phenol with a yield of 38%. Fe distributed over the surface of the coal had a pos. effect on the process. An increase in the Fe content to 4.7% resulted in the condensation of catechol to cokelike products. The addn. of steam inhibits the condensation.

5.90 Gasoline feedstock from bituminous coal. Everett Gorin (Consolidation Coal Co.). U.S. 3,018,241, 23 Jan 1962, Appl. 10 Oct 1960. Partial conversion of coal to H-rich liquids, suitable for gasoline feedstock, is made more selective by soln. under noncoking conditions by adding H from H-transferring solvents, b. 260-425°, such as Tetralin, Decalin, biphenyl, methyl- and dimethylnaphthalene, or mixts. from the process to dissolve 60% of the moisture- and ash-free (MAF) coal and < 80% where the H cost is prohibitive. Carbonization of the sepd. residue gives addnl. condensate besides the ext. for catalytic hydrogenation to a gasoline feedstock, b. < 360°. Thus, from 100 lb. of MAF Pittsburgh Seam coking bituminous coal extd. at 348° with Decalin, 23.0 lb. of ext. and 74.9 lb. of residue were obtained. Carbonization at 510° yielded 58.5 lb. char and 12.6 lb. tar, and hydrogenation at 440°, and 3500 lb./sq. in. over 15% MoO_3, 3% CoO, 82% Al_2O_3 gave 25.8 lb. of 360° gasoline feedstock consuming 1.46 lb. H. U.S. 3,018,242. High-volatile bituminous coal (> 20% by wt. volatile compd.) is converted to a H-enriched liquid and a char by a series of steps: Solvent extn. with a H-transferring solvent to ext. 50-70% by wt. of the MAF coal; sepn. of ext. and residue; carbonization of the latter at 425-760° to a char and a condensate that is fractionated to a < 325° gasoline feedstock and a > 325° fraction for catalytic hydrogenation to a feedstock; and topping of the ext. into the same fractions. Thus, a Pittsburgh Seam coal was extd. at 380° and 70 lb./sq. in. with a 260-425° recycle fraction (1:1) for 1 hr. to give a 57.8% by wt. ext. and 34.9% residue yield on the MAF coal. Fluidized carbonization of the residue at 510° and 20 min. residence time yielded 78.0% by wt. char and 16.8% tar plus light oil, based on the MAF residue. Catalytic hydrogenation of ext., tar, and light oil, b. > 325°, at 441°, and 3500 lb./sq. in. over MoS_2 yielded C_1-C_3 12.5, C_4 5.2, and C_5 325° distillate (80.6% by wt., based on fresh feed).

5.91 Catalytic hydrogenation of carbonized coal gases. Richard C. Perry and Charles W. Albright (Union Carbide Corp.). U.S. 3,231,486 (Cl. 208-8), 25 Jan 1966, Appl. 16 Dec 1960; 5 pp. Gases produced by low-temp. coal carbonization are stabilized to form low-mol.-wt. tar products. Thus, particulate carbonaceous material, e.g. coal, was mixed with H preheated to 400° at 400 psi. and passed to a carbonization zone where the material was heated to 500-50°. The resulting char was removed from the carbonization zone and the gases from the carbonization were passed over a catalyst contg. Ni 0.5, Co 1.0, and Mo 8.3 parts by wt. on an Al_2O_3 support at 425° and 400 psi. The vapors were then condensed. Uncondensed gases were mixed with fresh H and recycled to the carbonization zone.

1958

5.92 Recovery of quinoline from coal-hydrogenation products. Donald J. Foster and Denvil E. Reed (Union Carbide Corp.). U.S. 2,999,794. Appl. 24 Sept 1958. Quinoline (I) is recovered by azeotropic distn. from a mixt. of aromatic N-contg. compds. (II) obtained by liquid-phase hydrogenation of coal. Thus, to II (b.p. $\sim$235-41°) 500 g. in a 2-l. still pot, equipped with a 2-ft. packed column, kerosene (b.p. $\sim$223-30°) 500 g. was added with stirring. The mixt. was distd. to give a product (b_{20} 110-15°) contg. about 32% by wt. aromatic N bases and 68% kerosene. On cooling to approx. 5°, two layers sepd. Fractional distn. of the quinoline-rich, bottom layer gave I 117g.; b. 237°, overall yield $\sim$86%. Examples also describe the use of 1:2 wt. ratios of II to kerosene.

5.93 Hydrogenating refining of tars, tar oils, and coal-hydrogenation products. Paul Lehmann, Hermann Blume, and Emanuel Pindur. Ger. (East) 20,413 (Cl. 12o). Appl. 11 May 1958. The title products are hydrogenated at $>330°$ and ≤ 200 atm. in the presence of a sulfide of Mo, W, and Ni on an active Al_2O_3 carrier with a Mo:W:Ni ratio between 1:3:2 or 1:6:4. The catalyst permits hydrogenation at lower temps. Thus, 10 kg. active Al_2O_3 pellets was impregnated with 570 g. MoO_3 in 10% NH_4OH, dried, heated at 400° for 4 hrs., and impregnated 3 times with 12.51.20% NH_4OH contg. 2720 g. WO_3 and 2240 g. $NiSO_4$-$7H_2O$. Then the pellets were dried, heated again at 450° for 8 hrs. in a stream of H and H_2S, ground, mixed with 1% graphite, and pelletized to give a catalyst contg. MoS_2 4.4, WS_2 20.3, NiS 5.0%, Al_2O_3, and H_2O. Tar contg. 2100 mg./l. NH_3 and 15-17% phenol was hydrogenated at 356°, 200 atm., and a rate of 0.38 vol. tar/vol. catalyst/hr. to give a product contg. 5 mg./l. NH_3 and 0.04% phenol. The aniline point was 62.7°, and the color value 0.5.