

## 6. Acid/Base Systems

### A. Acids

1973

6.1 94611f Coal conversion. Masciantonia, Philip X.; Schowalter, Kenneth A. (USS Engineers and Consultants, Inc.) Ger. Offen. 2,259,542 (Cl. C 10g, B 03b), 14 Jun 1973, US Appl. 205,248, 06 Dec 1971; 63 pp. A 2-stage process is described. In the 1st desulfurizing and coking stage, finely divided coal is suspended in a liq. coke-oven product, heated to 871°, and stirred in contact with H-contg. gas contg. 2 Vol. % H<sub>2</sub>S and practically free of O to produce metallurgical coke. In the 2nd stage, finely divided coal is liquefied with H at 427-516° under 141-703 atm. pressure. The gases from the 2 processes are combined and the H removed and recycled. The light liq. fractions are removed from the combined products and the middle and heavy fractions are used as solvents in the 2nd stage. The raw materials may also include coal high in ash or S and may be predried. The temps. of the 1st stage vary between 482 and 871° and the pressure is held at 6.3-21.1 atm. The H donor for the 2nd stage may be the gas from the 1st stage. The major products are NH<sub>3</sub>, S, C<sub>2</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>10</sub>H<sub>8</sub>, gasoline PhOH, coke, o-, m-, and p-cresol, mixed xylenes, pyridine,  $\alpha$ -picoline, PhNH<sub>2</sub>, and creosote oil.

6.2 94602d Compounds separated from depolymerized brown coal. Imuta, Kazutoshi; Ouchi, Koji (Natl. Res. Inst. Pollut. Resour., Kawaguchi, Japan). Fuel 1973, 52(3), 174-80 (Eng). A demineralized Japanese brown coal was treated at 185° for 10 hr with phenol and p-toluenesulfonic acid as catalyst, steam distd., and filtered, yielding 121% of a solid product; this was extd. at the b.p. by a 1:1 by vol. EtOH-C<sub>6</sub>H<sub>6</sub> mixt., the sol. product methylated, and the yield of methylated product sol. in petroleum ether (14% of the depolymd. coal) was examd. by liq. and gas chromatog. The formulas of several cryst. substances that were isolated were detd. completely or partially. One was identified as 4,4'-dimethoxydibenzyl and another is believed to be 2-(2-methoxyphenyl)benzofuran. Others had been previously sepd. Two other compds. (0.42% of the depolymd. coal) were also sepd. and their structure approx. detd. The total characterized was 4.8% of the depolymd. coal and the total sepd. ~6.0%. From these results, suggestions are made concerning the depolymer. mechanism and the structure of the coal.

6.3 7734g Catalysts for the depolymerization of mature coals. Ouchi, Koji; Imuta, Kazutoshi; Yamashita, Yasumasa (Coal Carbon Div., Natl. Res. Inst. Pollut. Resour.,

Kawaguchi, Japan). Fuel 1973, 52(2), 156-7 (Eng). A no. of catalysts were assessed by comparing extn. yields, with pyridine and C<sub>6</sub>H<sub>6</sub>-EtOH, from the products after reacting a medium-volatile Japanese coal with phenol for 6 and 24 hr at 185° and for 6 hr at 95°. The best proved to be benzenesulfonic acid, p-toluenesulfonic acid, p-phenolsulfonic acid, and concd. H<sub>2</sub>SO<sub>4</sub>.

## 1972

6.4 156547p Effect of solutions of chemically active substances on the rate of gas emission by coal. Vasyuchkov, Yu. F.; Nozhkin, N. V.; Petrovskaya, E. A. (Mosk. Gorn. Inst., Moscow, USSR). Khim. Tverd. Topl. 1972, (2), 137-40 (Russ). Treatment of Karaganda coal samples (50-100  $\mu$ ) (evacuated at 0.1-0.5 torr and satd. with CH<sub>4</sub> at 8-10 atm) with aq. 0.1N acid or salt solns. increased the rate of gas emission by coal at 22°. The effectiveness of the compds. used in accelerating the gas emission decreased in the order: HCl, oxalic acid, citric acid, CuCl<sub>2</sub>, BaCl<sub>2</sub>, NH<sub>4</sub>Cl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NaCl, AlCl<sub>3</sub>. According to petrog. anal., HCl penetrates vitrinite preferentially at the contact sites of carbonates with coal, whereas in fusinite it dissolves all the carbonates present in the pores. Free pores and fissures thus formed in the coal enhance the penetration of acid solns. as well as CH<sub>4</sub> emission by the coal.

## 1970

6.5 68464r Extracting sulfur compounds from coal. Meyers, Robert Allen (TRW Inc.) Ger. 2,108,786 (Cl. C 10c), 12 Apr 1973, US Appl. 13,745, 24 Feb 1970; 7 pp. The org.-S content in coal was decreased by extn. with solvents, esp. o-chlorophenol, H<sub>3</sub>PO<sub>4</sub>, or HPF<sub>6</sub>. Thus a -150 mesh coal contg. 4% S extd. 2 hrs at 150° with o-chlorophenol contained 3.2% S.

131553d Solvent extraction of organic sulfur and nitrogen compounds from coal. Meyers, Robert A. (TRW Inc.) Ger. Offen. 2,108,786 (Cl. C 10c), 16 Sep 1971, US Appl. 24 Feb 1970; 20 pp. Org. S compds. were extd. up to 30-50% from coal at 150° with o-chlorophenol, phenol, HPF<sub>6</sub>, or NaOH after treatment with HCl. Org. N compds. were removed up to 90% by extn. with 85% H<sub>3</sub>PO<sub>4</sub> at 100-50°. Thus, 1 part of Missouri coal contg. 2% org. S was agitated with 5 parts of o-chlorophenol for 2 hr at 150°, filtered, and dried to give a coal with no change in BTU value and 3.2% S content (40% redn. of org. S).

1968

6.6 123751q Coal liquefaction. Gatsis, John G. (Universal Oil Products Co.) U.S. 3,503,863 (Cl. 208-8; C 10g), 31 Mar 1970, Appl. 29 Mar 1968; 4 pp. Coal and solvent in the presence of  $H_2S$  yield liq. hydrocarbons from the coal ext. Thus, 1 part eastern Kentucky stoker coal and 3 parts methyl-naphthalene was run in a colloid mill 5 hr, and 447 g of the mixt. in a rocker autoclave at 10 atm  $H_2S$  and 90 atm H (total 100 atm) was heated to  $390^\circ$  and the pressure increased to 200 atm for 2 hr to give by filtration and distn. 80 g liquefied coal and 17 g solid residue. The conversion of solid coal to liq. was 87.66% by wt.

1967

6.7 42131c Progressive depolymerization of coals. K. Ouchi (Div. Mineral Chem., C.S.I.R.O., Chatswood, Australia). Fuel (London) 46(4-5), 319-22 (1967) (Eng). The changes in properties of the reaction products during successive depolymns. are described. Yallourn brown coal (67.9% C) and the vitrain of bituminous coal from the Fiery seam (86.7% C) were ground, dried, and depolymd. in a refluxing soln. of p-toluenesulfonic acid (contg. 10%  $H_2O$ ) and phenol under N. After removal of the PhOH by steam distn., the product was dried and extd. with 7:3  $C_6H_6$ -EtOH. The dissolved material was recovered by steam distn. of the solvent, and the insol. part was used for the next depolymn. reaction. For the Yallourn coal, the C content of the ext. increased during successive depolymns., but for the Fiery coal it decreased. The phenol mols. are added at cleavage sites during depolymn., and the depolymn. results indicate that the insol. part of the product has a more and more dense network structure at fewer reactive sites and the phenol mols. accumulate. The ir spectra are clearer in the exts. and residues than in the raw coals and show that aliphatic structures increase in the exts. as the depolymn. proceeds. The absorption due to  $CO_2H$  groups decreases in the exts. with increasing depolymn. After depolymn., a large part of the coals dissolves in  $C_6H_6$ -EtOH and pyridine. The addn. of PhOH occurred at the ortho or para position.

1965

6.8 Catalytic depolymerization of coals. II. Depolymerization of various coals in phenol by using p-toluenesulfonic acid as a catalyst. K. Ouchi, K. Imuta, and Y. Yamashita (Resources Res. Inst., Kawaguchi, Japan). Fuel 44(3), 205-9 (1965) (Eng); cf. CA 62, 11584f. Coals of different rank were allowed to react with phenol with p-toluenesulfonic acid as

catalyst; the resulting wt. increases and soly. in pyridine and  $C_6H_6$ -EtOH were measured. Mol. wts. of the products, calcd. from the percentage increase in wt. for coals of increasing rank in the range 70-93% C, increased gradually from about 300 to 1100. The products from most of the coals were almost entirely sol. in pyridine, and the degree of extn. with  $C_6H_6$ -EtOH decreased regularly with increasing rank from lignite to anthracite.

6.9 Catalytic depolymerization of coals. I. Depolymerization of Yubari coal by p-toluenesulfonic acid as catalyst. K. Ouchi, K. Imuta, and Y. Yamashita (Higengijutsu Shikenjo, Resources Res. Inst., Kawaguchi, Japan). Fuel 44(1), 29-38 (1965) (Eng). Yubari coal was treated at various temps. with p-toluenesulfonic acid (I) in PhOH. Extensive depolymerization occurred and the soly. in pyridine and in  $C_6H_6$ -EtOH increased. The mol. wt. calcd. from the satd. wt. was  $\sim 350$ , which agreed with exptl. values for the pyridine-sol. materials. Vacuum-heating of the reaction products gave a new peak on the lower temp. side in the thermobalance differential curve and increased the amt. of solid tar distg. in vacuo at lower temps. The OH content of the coal reacted also increased, but dehydration took place simultaneously. Analysis of the reaction kinetics gave an activation energy of  $\sim 33$  kcal./mole. The extent of the reaction increased with increasing I addns.

6.10 Catalytic depolymerization of coals. I. Kazutoshi Imuta, Yasumasa Yamashita, Koji Ouchi, and Hideo Tanaka (Resources Res. Inst., Mituuroko, Japan). Nenryo Kyokaishi 44(460), 582-90 (1965) (Japan). The effect of sulfonic acid-phenol catalysts on the depolymerization of coal was studied.

#### 1964

6.11 53448h Coal extracts. Hazeldine, Robert N.; Banks, Ronald E. (Coal Industry [Patents] Ltd.) Brit. 1,118,629 (Cl. C 10 1), 03 Jul 1968, Appl. 30 Oct 1964; 3 pp. Coal (200-300 B.S. mesh) is extd. with 10-20 times its wt. of anhyd. HF at 100-200° under 80-120 atm. for 15-20 hrs. The cat. may be used in soln., or the HF may be distd. before further reaction. Coal is more sol. in org. solvents, such as, cyclohexanone (I),  $C_6H_6N$ ,  $HCONMe_2$ ,  $Et_3N$ ,  $PhNO_3$ , or  $PhNHNH_3$ , after HF pretreatment, esp. when the pretreatment is carried out in an atm. of O. Thus, West Cannock coal (10 g.), ground to  $<240$  B.S. mesh, and 200 g. anhyd. HF were charged into a stainless-steel autoclave. O was then admitted at a pressure of 200 atm., and the autoclave agitated for 17 hrs. at 100°. The O was vented and the HF distd. under reduced pressure. The residue (10 g.) was extd. with boiling I to give a soln. that was evapd. to yield 3.2 g coal ext. The % by wt. of material extd. from Hemsworth Haigh

coal by various treatments was as follows: 2% in HF at 20°; 11% in I at 157°; 13% in I at 157° after pretreatment with HF at 20°; 21% in I at 157° after pretreatment with HF at 150°; 25% in I after pretreatment with O-HF at 100°.

1963

6.12 Identification of isopropyl groups of aromatic structures in bituminous coal. L. A. Heredy, A. E. Kostyo, and M. B. Neuworth (Consolidation Coal Co., Library, Pa.). Fuel 42, 182-4 (1963). Recent studies on the compn. of products from low-temp. depolymerization of a bituminous coal with C<sup>14</sup>-labeled phenol-BF provide strong evidence for the existence of iso-Pr side chains. The alkylphenols obtained by extn. with C<sub>6</sub>H<sub>6</sub> and fractionation were examd. by gas-liquid chromatography, nuclear magnetic resonance, and infrared spectrometry. The largest single constituent, representing nearly 1/2 of the mixt., was p-isopropylphenol. The C<sup>14</sup> assay of this compd. showed that it was formed by Pr-group transfer from coal to the tagged phenol. Evidence is given that the isopropylphenols were present in the coal as such and not formed by isomerization of n-Pr groups.

## B. Bases

1972

6.13 128744c Successive treatment of coals with sodium in liquid ammonia. Angelova, G.; Kovacheva, V. (Inst. Obshch. Neorg. Khim., Sofia, Bulg.). Khim. Tverd. Topl. 1972, (4), 29-38. Successive treatment of coals with sodium in liquid ammonia. Four coals of different degree of metamorphism were extracted with pyridine and then treated with sodium in liquid ammonia to break ether bonds of the aryl-aryl and benzyl-aryl type. After extraction of low molecular digestion products, the residue was treated again with sodium and so on, repeating the procedure three times. The total yield of pyridine extract amounted to 88-89% of the organic matter in high-sulfur coals and was much lower for lean and gas coals. The chloroform-soluble and insoluble fractions of the pyridine extract had a condensed aromatic structure with an average of 4-10 and 10-35 rings, respectively. In coking coals and rush coals, the main structural components are bound by aryl and benzene-aryl ether and thioether bonds. The formation of low-mol.-wt. compds. during the thermal treatment may be attributed to the cleavage of C-O-C and C-S-C bonds and thermophys. sepn. of low-mol.-wt. compds. bound by the weak H bond.

## 1970

6.14 101996d Dissolving bituminous coal. Seitzer, Walter H. (Sun Oil Co.) U.S. 3,642,607 (Cl. 208/8; C 10g), 15 Feb 1972, Appl. 63,334, 12 Aug 1970; 3 pp. A mixt. of powd. coal, a donor solvent oil, CO, H<sub>2</sub>O, and an alkali metal hydroxide or its precursor (NaCl, K oxalate, Rb<sub>2</sub>CO<sub>3</sub>, NaOAc, Na<sub>2</sub>CO<sub>3</sub>, or CsNO<sub>3</sub>) is heated at 400-500°/4000-6000 psig. The coal is 87-100% solubilized in 0.5-3 hr and the liq. obtained subjected to normal refinery methods to provide liq. fuels. The H donor solvent oils are partially hydrogenated aromatic hydrocarbons, e.g., anthracene oil. The oil-coal ratio is 1:1.

## 1965

6.15 Reduction of coal by lithium-ethylenediamine and reaction of model compounds with methylamine systems. Leslie Reggel, Charles Zahn, Irving Wender, and Raphael Raymond (U.S. Bur. of Mines, Pittsburgh, Pa.). U. S., Bur. Mines, Bull. No. 615(4), 57 pp. (1965) (Eng). A series of vitrains contg. 67.9-93.1% C and a natural graphite were reduced on a small scale by the Li-ethylenediamine system (I) at 100°. Coal is very reactive at 100° and adds large amts. of H. Even a high-rank coal and graphite, which are very difficult to hydrogenate catalytically at high temps. and pressures, were reduced by I. Studies on model compds. consisted of redn. of hydrocarbons and oxygenated compds. with I, isomerization of olefins and dehydrogenation of cyclic dienes by N-lithioethylenediamine, reductive dimerization of naphthalene by Na-ethylamine, and formation of imidazole derivs. and cleavage of C-C bonds by N-lithioethylenediamine and N-sodioethylenediamine.

6.16 Pyrolysis kinetics of a Utah coal with discussion of lithium reduction and batch hydrogenation. Norbert John Kertamus (Univ. of Utah, Salt Lake City). Univ. Microfilms (Ann Arbor, Mich.), Order No. 65-1791, 128 pp.; Dissertation Abstr. 26(0), 5172 (1965) (Eng).

6.17 97312b Some properties of petrographic micro-components of humic coals. I. V. Eremin, V. I. Zabavin, and L. A. Kleimenova. Mater. Soveshch. Rab. Lab. Geol. Organ., 9th, Kiev 1965, 31-8 (Russ). The degree of metamorphism influences the amt. and compn. of the hydrolytic distintegration products (HDP) obtained on heating the org. coal substance with KOH in a mixt. of alc. and pyridine. The yield of HDP from coals of the II and III stages of metamorphism was almost const. for each stage, irresp. of the amt. of microcomponents (fusinite and 2/3 of semivitrinite groups) present up to 45%

but was reduced considerably upon further increases in the amt. of microcomponents. The II<sub>2-3</sub>-stage coals (microcomponents  $\leq 32\%$ ) yielded a max. amt. of HDP (32-4%). The amt. of acidic constituents in the HDP decreased from 7-11% in the II<sub>1-2</sub>-stage coals to 2-4% in the II<sub>2-3</sub>-stage coals, and to traces in the III-stage coals. The IV-stage coals (microcomponents 16-60%) were almost unaffected by hydrolysis (HDP yield  $\leq 3\%$ ). As a consequence of the hydrolysis, wedge-shaped fissures with even surfaces developed on the microcomponents of vitrinite and fusinite groups in the I-, II-, and II<sub>1-2</sub>-stage coals. In the II<sub>2-3</sub>- and III<sub>2</sub>-stage coals, mostly the less-stable vitrinite group constituents were dissolved or pitted; the HDP were mostly or wholly neutral. The solvents easily penetrated the I- and II-stage coals, which was evident from the alterations noticeable even in the central parts of large coal grains (0.2-0.25 mm.). This was the result of the swelling of these coal substances in pyridine. The III-stage coals were less penetrable, and only the peripheral regions of the grains were attacked.

1964

6.18 Catalytic dehydrogenization of coal. II. Reversibility of the dehydrogenation and reduction of coal. L. Reggel, I. Wender, and R. Raymond (Bur. of Mines, Pittsburgh, Pa.). Fuel 43(3), 229-33 (1964); cf. CA 57, 14089c. The "reversibility" of the redn. of coal (Li ethylenediamine at 110°) and of the dehydrogenation of coal (Pd as a catalyst and phenanthridine as vehicle at 347°) is discussed in detail. H added to coal by redn. can be completely removed by dehydrogenation, but H removed from coal by dehydrogenation can be only partly restored by redn. Coal can evidently serve as both a H acceptor and a H source, its chief role depending on its rank.

6.19 Reduced coals. I. Mechanism of coal pyrolysis. A. C. Bhattacharyya, B. K. Mazumdar, and A. Lahiri (Central Fuel Res. Inst., Jealgora, India). Fuel 43(3), 181-8 (1964). The mechanism of coal pyrolysis (600°) advanced earlier (CA 56, 14540g) is reexamd. on the basis of parallel studies on coals, including a semicoke sample, reduced with Li and ethylenediamine. The addnl. C volatilized during pyrolysis is equiv. to the aromatic C made hydroaromatic during redn., affording direct proof of the selective and complete volatility of nonaromatic structure of coal during pyrolysis.

6.20 Reduction of coal by lithium-ethylenediamine at room temperature. H. W. Sternberg, C. L. Delle Donne, L. Reggel, and I. Wender (Bur. of Mines, Pittsburgh, Pa.). Fuel 43(2), 143-6 (1964). Four vitrains and a graphite were reduced with Li in ethylenediamine at room temp. The starting materials were identical with those used for Li-ethylenediamine

redns. at 100°. Although the amt. of H taken up at room temp. was about half that at 90-100°, the pattern of H uptake was the same, i.e., in going from low- to high-rank coals, H uptake reached a max. with the Pocahontas vitrain. An unexpected result was the discovery that Bruceton vitrain reduced at room temp. was as sol. as when reduced at 90-100°, although considerably less H was added at the lower temp. From results of the hydrogenation of coronene, room-temp. redn. of condensed aromatic systems can apparently lead to products with isolated double bonds.

### 1963

6.21 Electrochemical coal reduction. Raymond E. Markby, Heinz W. Sternberg, and Irving Wender (U. S. Bur. of Mines, Pittsburgh, Pa.). Nature 199(4897), 997 (1963); cf. CA 58, 10970g. The electrolytic redn. of coal in ethylenediamine makes it more sol. in pyridine than chem. redn. where possibly polymerization at the more elevated temp. occurs, making it thus less sol.

### 1961

6.22 Reduction of coal by lithium ethylenediamine. Series of vitrains. L. Reggel, R. Raymond, W. A. Steiner, R. A. Friedel, and I. Wender. Fuel 40, 339-56 (1961). A series of vitrains contg. 67.9-93.1% C (moisture- and ash-free basis) and a graphite were reduced with Li ethylenediamine, resulting in addn. of H, H<sub>2</sub>O, and ethylenediamine to the vitrain. The max. H addn. was obtained with vitrain contg. 90% C when 55 H atoms were added per 100 C atoms. More than half of the C atoms in this vitrain are involved in C:C double bonds. H addn. increases with decreasing vitrain sample size. While the reduced vitrains are more sol. in pyridine than the starting materials, the pyridine soly. was not proportional to the extent of H addn. One of the vitrains (88.7% C) was 97% sol. in pyridine. Infrared and ultraviolet spectra of the reduced vitrains showed changes consistent with addn. of H and redn. of aromatic rings. The reduced vitrains contained fewer free radicals than the starting vitrains. Since the "H<sub>2</sub>O" added to a vitrain is not removed at 100° and 1 mm., it is presumed that this "H<sub>2</sub>O" may consist of H<sub>2</sub>O mols. firmly held by some type of chem. binding force, or it may no longer consist of discrete H<sub>2</sub>O mols. Two mechanisms are probably involved for most vitrains: one involving the O of the vitrains, the other involving the C and H; only the latter can be operative for graphite.



1959

6.23 Reduction of coal by lithium-ethylenediamine. Series of vitrains. Leslie Reggel, Raphael Raymond, and Irving Wender (U. S. Dept. of the Interior, Pittsburgh, Pa.). Am. Chem. Soc. Div. Gas Fuel Chem., Preprints Apr. 1959, Vol. 2, 177-90. Seven low-ash vitrains (77-91% C) were reduced with Li in ethylenediamine. The products were examd. by infrared and ultraviolet spectroscopy, x-ray diffraction, electron paramagnetic resonance, soly. in pyridine, and ultimate analysis. Pyridine soly. of the materials was greatly increased. The extent of redn. increased with increasing rank of the vitrains, reaching a max. at ~90% C, and then decreased. The largest amt. of H added was 44 atoms/100 C atoms in the starting vitrain. Most of the S was removed from the vitrains during the redn. Treatment of a graphite with Li-ethylenediamine resulted in addn. of a considerable amt. of H.

C. Halides (Lewis Acids)

1973

6.24 106679z Economics of the production of gasoline, fuel oil, and aromatic chemicals from coal by hydrogenation. Qader, S. A.; Duraiswamy, K.; Wood, R. E.; Hill, G. R. (Dept. Min. Metall. Fuels Eng., Univ. Utah, Salt Lake City, Utah). AIChE Symp. Ser. 1973, 69(127), 102-4 (Eng). Additional data considered in abstracting and indexing are available from a source cited in the original document. In a coal hydrogenation plant operating at 650°, 2000 psi H pressure, 10 g/min coal feed rate, and a H flow of 90 l./min with ZnCl<sub>2</sub> as the hydrogenation catalyst the coal conversion was 70%. The liq. product had an API gravity of 11.5° and contained S 0.64, N 0.76, O 2.80 wt. %, asphaltene 21.0 vol. %. The distn. yielded light oil (b. 80-200°) 18.0, middle oil (b. 200-350°) 57.0, and heavy oil (b. >350°) 25.0 vol. %. The gas contained H 94.0, CH<sub>4</sub> 5.0, ethane 0.5, and propane 0.5 vol. %.

6.25 55735e Coal hydrogenation using a potassium chloride-zinc chloride molten salt mixture as a catalyst. Berg, Lloyd; Malsam, John S. (United States Dept. of the Interior) U.S. 3,736,250 (Cl. 208-10; C 10g), 29 May 1973, Appl. 199,764, 17 Nov 1971; 2 pp. KCl is incorporated with molten ZnCl<sub>2</sub> in a coal or coal ext. hydrocracking zone so that any reaction product and unreacted feedstock entrained in the catalyst can be sepd. from the spent catalyst in a simple gravity sepn. vessel. The incorporation of KCl with the molten ZnCl<sub>2</sub> in a mole ratio of 1:1 allows the lighter entrained hydrocarbon phase to readily sep. out from the heavier spent

molten salt phase so as to form 2 adjacent layers. To realize at least an 80% conversion of the feedstock, the operating temp. is about 400° and a pressure of 2500 psig. During catalyst regeneration, the spent molten salt and entrained hydrocarbon phase from the hydrocracking zone are conveyed to a gravity settling zone to allow the heavier molten salt phase to settle out.

6.26 94546p Increase in extractability of bituminous coals caused by Friedel-Crafts acylation. Hodek, Werner; Koelling, Georg (Bergbau-Forsch. G.m.b.H., Essen, Ger.). Fuel 1973, 52(3), 220-5 (Eng). Four bituminous coals of different rank were acylated with aliph. acyl chlorides by using Friedel-Crafts catalysts; a dry steam coal and a coking coal showed esp. good reactivity, 5 acyl groups being combined per 100 C atoms. Compared with the initial coal, the acylated coals were distinguished by considerably larger amts. sol. in pyridine and other solvents. About 85% of the coking and dry steam coal became sol. when acylated with lauroyl chloride or acyl chlorides having longer chains. The extractability of the coals after acylation depends on the chain length of the added acyl groups. The exts. are apparently dispersed in the soln. in mol. form. The good extractability of acylated coals seems to be mainly due to depolymn. of the coal substance during acylation, removal of H bridges by esterification of the phenolic OH groups, and diminution of intermol. forces between the arom. structures by insertion of long-chain substituents.

6.27 7758t Kinetics of conversion of tetralin during hydrogenation of coal. Potgieter, Hendrik G. J. (Dept. Ind. Chem., Univ. Potchefstroom, Potchefstroom, S. Afr.). Fuel 1973, 52(2), 134-7 (Eng). Expts. with 2 catalysts suggested that the conversion of Tetralin during the hydrogenation of coal, mainly to naphthalene, may be either a reversible or a nonreversible reaction depending on the catalyst employed.  $\text{SnCl}_2$ , although considered one of the best coal hydrogenation catalysts, is inferior to  $\text{Co}_2\text{O}_3$  when the side reaction Tetralin  $\rightarrow$  Decalin and the rate of dehydrogenation of Tetralin are considered.

## 1970

6.28 78196r Liquefaction of some western coals. Wood, Ralph E.; Anderson, Larry LaVon; Hill, George Richard (Dep. Mineral Eng., Univ. Utah, Salt Lake City, Utah). Quart. Colo. Sch. Mines 1970, 65(4), 201-16 (Eng). The liquefaction of two Utah coals was investigated for 0.08- to 0.33-sec residence times in a free-fall reactor at 2000 psig H and 400 to 700°. Pre-treatment of the feed by surface oxidn. reduced the buildup of

solids in the reactor, but also decreased the conversion.  $\text{ZnCl}_2$  as the catalyst is easier to add to the coal and easier to recover than  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , but the  $\text{ZnCl}_2$  gives 2-3% lower conversions. The  $\text{ZnCl}_2$  at  $578^\circ$  gave 73-9% total conversions with 48-59% conversion to liqs.

6.29 68468v Hydrogenation catalyst. Kiovisky, Thomas E.; Wald, Milton M. (Shell Oil Co.) U.S. 3,725,239 (Cl. 208-10; C 10g), 03 Apr 1973, Appl. 37,912, 15 May 1970; 2 pp. Division of U. S. 3,663,452 (CA 77:52827j). The catalyst is a complex salt of a chloride, bromide, or iodide of Zn, Sn, Sb, Bi, Cd, Ga, Hg, or As, and the corresponding ammonium halide [e.g.  $(\text{NH}_4)\text{HgI}_3$ ]. Coal is hydrogenated by such a catalyst to yield a liq. product essentially free of O, S, and N. Thus, a catalyst  $(\text{NH}_4)_2\text{SbBr}_5$  (238 g) converted 40 g of Illinois No. 6 coal to product b.  $250^\circ$  in 60 min at  $350^\circ$  and 1800 psi, using 5.8 g H/100 g coal.  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  are by-products.

6.30 122238m Coal hydrogasification catalyzed by aluminum chloride. Kawa, Walter; Friedman, Sam; Frank, L. V.; Hiteshue, Raymond W. (U.S. Bur. Mines, Pittsburgh, Pa.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1968, 12(3), 43-7 (Eng).  $\text{AlCl}_3$  in high concns. catalyzes the hydrogenation of high-volatile A bituminous coal to hydrocarbon gases. In a batch reactor at 4000 psi and  $450^\circ$ , a hydrocarbon gas yield of 68% (based on wt. of moisture- and ash-free coal) was obtained;  $<1\%$  oil was produced. Product distributions from hvab coal were detd. at  $250$ - $450^\circ$  using equal wts. of coal and catalyst, and the effect of catalyst concn. on yields was examd. at  $300^\circ$ . Considerable reaction of coal occurred at temps. below its softening point. Thus it may be possible to catalytically hydrogasify coal at low temps. in a continuous system without incurring agglomeration. Expts. were also made with higher and lower rank coals, tars, and a petroleum residue. The amenability of a carbonaceous material to catalytic hydrogasification increases with increasing H content and decreasing O content.

6.31 47222w Studies on use of melted salts of metals as catalysts for hydrogenation and cracking of carbon peptizates. I. Catalytic properties of melted zinc chloride. Czarny, Zdzislaw; Olpinski, Wofciech; Tengler, Szczepan (Główny Inst. Gorn., Katowice, Poland). Rocz. Chem. 1970, 44(1), 165-71 (Pol). Carbon peptizate contg. 91.52 C, 5.60 H, 0.02 N, 0.34 S, and 1.62% O was mixed with  $\text{ZnCl}_2$  catalyst in an autoclave and heated to  $450^\circ/85$  atm. The resulting mixt. was analyzed by the gas chromatog. With increasing  $\text{ZnCl}_2$  content in the mixt. from 0 to 40 wt. %, the content of hydrocarbon fraction b.  $\leq 280^\circ$  increased from 6.6 to 19.6 and that of all boiling fractions from

60.2 to 81.6%, whereas the content of nondistd. residue decreased from 39.8 to 18.4 wt. %. The content of hydrocarbons in gases increased from 1.6 to 25.18 vol. %.

6.32 119817k Catalytic hydrogenative cracking of carbonaceous material. Wald, Milton M.; Hardesty, Donald E.; Rodgers, Thomas A.; Klovsky, Thomas E.; Petzny, Wilfried J. (Shell Internationale Research, Maatschappij, N. V.) S. African 70 04,096, 26 Jan 1971, Appl. 16 Jun 1970; 48 pp. Liq. metal halides are used as a continuous phase catalyst in the hydrocracking of petroleum residues and other heavy hydrocarbons. Typical of these catalysts are antimony tribromide, zinc chloride, and mercuric iodide. The residue is mixed with H and passed up through a molten pool of the metal halide under hydrocracking conditions. To prevent buildup of coke, metal contaminants and ammonium complexes, a slip stream of the catalyst is removed and regenerated.

6.33 Catalytic carbonylation of coals. R. N. Smirnov (Inst. Fossil Fuels), Kh T T #6:50-57 (1970). The carbonylation of coals in sulfuric acid with formic acid in the presence of  $AlCl_3$ ,  $ZnCl_2$  and/or  $(CH_3)_2CHOH$  as catalysts is accompanied by sulfonation. The carbonylation products react more readily with water, than do the original coals. They are also more readily oxidizable. The carbonylation products of Babaco coal, unlike those from other coals, after reaction with water comprise resin-like soluble products. Tables, IR spectra and 18 references.

#### 1969

6.34 14504r Thermographic study of the thermal degradation of coals in the presence of carbon tetrachloride, metals, and salts. Smirnov, R. N.; Chernykh, V. I. (USSR). Khim. Tverd. Topl. 1969, (5), 117-20 (Russ). A sealed rotating retort was used to study the pyrolysis of boghead coal and Podzhurinsky bright coal of type D in the presence of different reagents. The differential heating curves show that  $CCl_4$ ,  $Hg_2Cl_2$ ,  $AlF_3$ , and  $ZnCl_2$  have a substantial effect on decompn. of the solid fuels. The effects of Na, Mg, Zn, B, and Al on the coals are much smaller.

6.35 103867h Coal can also yield liquid fuels. Qader, Shaik A.; Haddadin, R. A.; Anderson, Larry LaVon; Hill, George Richard (Univ. of Utah, Salt Lake City, Utah). Hydrocarbon Process. 1969, 48(9), 147-52 (Eng). Coking and agglomeration problems during coal hydrogenation were almost eliminated by mixing high-temp. coke, and highly volatile Utah coal in the ratio 1:1. It was necessary to use a fine particle size to avoid heat cond. loss, but pressure had little effect on gas

yield, and 2000 psi. was optimum for max. conversion.  $\text{SnCl}_2$  proved to be an excellent catalyst, effecting max. coal conversion of 75%, and  $515^\circ$  was the optimum for max. liq. product yield. This was somewhat similar to low-temp. tar. Hydro-refining of the liq. produced at  $420^\circ$  and 1500 psi. yielded 26% gasoline and 56% diesel oil. The gaseous product could be used as a substitute of natural gas.

6.36 108101t Fuels by hydrocracking oil from coal. Qader, Shaik A.; Hill, George Richard (Univ. of Utah, Salt Lake City, Utah). Hydrocarbon Processes. 1969, 48(3), 141-6 (Eng). Hydrocracking of crude oil obtained by coal hydrogenation over a dual-function catalyst is proposed to give regular or premium-grade gasoline, diesel oil, and jet fuel. Thus, crude oil was first prepd. by hydrogenation of a high-volatile bituminous coal from Utah by using a short residence time in a fluidized-bed reactor at  $510^\circ$ , a pressure of 2000 psia., and  $\text{SnCl}_2$  as catalyst. The asphaltenes were sepd. from the oil by extrn. with  $n\text{-C}_6\text{H}_{14}$  and the resulting deasphalted product used as a feedstock for a hydrotreating unit. This secondary process, if carried out at  $500^\circ$  and 2000 psia, yielded 70% gasoline of a 90 Research octane no. When the temp. was reduced to  $375^\circ$ , a 47% yield of diesel oil of 46 cetane no. was obtained. Two dual-function catalysts are described, one contg. 6% NiS and 19%  $\text{WS}_2$ , and the other contg. 3% Co oxide and 12%  $\text{MoO}_3$ , both supported on  $\text{SiO}_2\text{-Al}_2\text{O}_3$ . The reactor is discussed in detail as well as various methods for regenerating the catalysts. The activity of the catalysts was reduced considerably by coke deposition, although the original activity was regained after regeneration. Data are given showing the effect of reaction pressure, temp., space velocity, and catalyst compn. on the product distribution.

6.37 Thermographic study of thermal destruction of coals in the presence of  $\text{CCl}_4$ , metals, and salts. R. N. Smirnova and V. I. Chernykh (Inst. Fossil Fuels). Kh T T #5:117-20 (1969). Differential thermographic curves were obtained for decomposition of boghead coal in a rotary retort in the presence of  $\text{AlF}_3$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}$ ,  $\text{CCl}_4$ , B, Zn, Al, Mg and Na. The initial stage of the process apparently involves the addition of  $\text{CCl}_4$  to coal with well-defined exothermic effect at  $45^\circ\text{-}120^\circ\text{C}$  which predominates over the endothermic vaporization effect of  $\text{CCl}_4$  and which is quite unexpected. Lewis acids show an exothermic effect and substantially reduce the thermal stability of coal, probably via structural changes at  $100^\circ\text{-}180^\circ\text{C}$  to form complexes. Sodium, magnesium, zinc, boron, and aluminum had a much weaker effect. Diagram and curves.

1968

6.38 39669n Preparation of organosilicon compounds from coals and silicon tetrachloride. Smirnov, R. N.; Maksimova, T. P.; Chubarova, M. A. (USSR). Khim. Tverd. Topl. 1968, (6), 157-62 (Russ). Pyrolysis of coals performed in the presence of  $\text{SiCl}_4$  in a flow system in an inert atm. yielded gases, liqs., and a reactor residue as the reaction products. The coals used in expts. were Olenek boghead coal (BC) and Kuzbacs long-flame coal (LFC). The reactor residue was analyzed for Si and Cl (coal, final temp. of pyrolysis, % Si, % total Cl, % hydrolyzable Cl given): BC, 600°, 24.60, 9.30, 8.81; BC, 800°, 27.71, 6.15, 4.11; LFC, 1020°, 7.80, 1.90, 0.35; LFC, 1800°, 7.43, 1.03, 0. The Si-contg. products are polycarbon organosilicon compds. giving no SiC or graphite at 1800°. After distg. the unreacted  $\text{SiCl}_4$ , the liq. products contg. organosilicon compds. and some hydrocarbons were treated with EtOH to give the corresponding ethers which were fractionated and analyzed. The ethers contained no double bonds, OH or CO groups, and all higher fractions easily polymd. in the presence of aq.  $\text{H}_2\text{SO}_4$ . Some gaseous products were trapped in flasks with MeOH, EtOH, and  $(\text{CH}_2\text{OH})_2$ . The HCl formed was absorbed in a suspension of  $\text{CaCO}_3$  in  $\text{C}_6\text{H}_6$ . The untrapped gases were mainly  $\text{H}_2$ , paraffins, CO, and a small amt. of unsatd. hydrocarbons. The compds. trapped in  $(\text{CH}_2\text{OH})_2$  after the pyrolysis of BC were fractionated to give fractions b<sub>13</sub> 30-98° and 98-100°, resp., and a residue. In the case of LFC, only polymers were obtained from trapped materials. The amts. of products obtained in the pyrolysis of BC and LFC were, resp., 28.5% and 77.3% of the distn. residue, 65.0% and 33.3% of the distillate, and 45% and 104.2% of materials trapped in the flask with MeOH (the amts. are given with respect to the amt. of starting material). The organosilicon compds. formed during pyrolysis of coals in the presence of  $\text{SiCl}_4$  are believed to be alkylchlorosilanes and alkylsilanes.

6.39 70044m Activity test of hydrogenation catalysts under high pressure by differential thermal analysis. Ishii, Tadao; Sanada, Yuji; Takeya, Gen (Hokkaido Univ., Sapporo, Japan). Kogyo Kagaku Zasshi 1968, 71(11), 1783-7 (Japan). D.T.A. app. consisting of a twin-type autoclave with a capacity of ~60 ml. was used for a study of coal hydrogenation with various catalysts under 200 atm. This app. can be used up to 200 kg./cm.<sup>2</sup> and 500°. The activity of catalysts was compared effectively by using the temp. of an exothermic peak at ~300-450°, and the catalytic action was discussed on the basis of D.T.A. thermograms and x-ray diffraction analysis of the catalysts. The order of the catalytic activity was as follows [catalyst used, (catalyst compn. under reaction conditions, and temp. peak) given]:  $\text{ZnCl}_2$  ( $\text{ZnCl}_2$ , 329°) >  $\text{SnCl}_3 \cdot 2\text{H}_2\text{O}$

(—, 389°) > SnS (SnS + Sn, 372°) > SnO<sub>3</sub> (SnO<sub>3</sub> + Sn, 386°) > (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (MoO<sub>2</sub>, 390°) > red mud + S (—, 397°) > ZnO (ZnO, 401°) > red mud (—, 429°) = ZnS (ZnS, 420-35°) = no catalyst (420-36°). Metal compds. and temps. in parentheses indicate the chem. forms of the catalysts under the reaction conditions and the exothermic peak temps., resp. The kinetic data for coal hydrogenation with red mud + S, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, and SnCl<sub>2</sub>·2H<sub>2</sub>O were calcd. from the D.T.A. peaks by using Kissinger's method. The activation energy (40.8 kcal./mole) obtained by D.T.A. for the red mud + S was about twice that obtained by isothermal batch expts. with respect to the org. residue insol. in C<sub>6</sub>H<sub>6</sub>.

## 1967

6.40 101712x Pyrolysis of coals in carbon tetrachloride vapor. R. N. Smirnov, N. A. Pustovalova, and M. A. Chubanova. Khim. Tverd. Topl. 1967 (3), 134-9 (Russ). A Yakutya boghead and a Kuznetsk long-flame humic coal contg. C 80.92 and 79.0, H 10.62 and 5.6, and volatile matter 85.1 and 44.0% (based on combustible matter), resp., were pyrolyzed in CCl<sub>4</sub> vapor according to the method described in U.S.S.P. 170,038 (CA 63:6759e). The pyrolysis yielded 36.2 and 77.3% of solid residue and 350 and 190% liquid products for the boghead and the long-flame coal, resp., and a large amt. of gases contg. chiefly HCl, CO, and CH<sub>4</sub>. The liquid products were rectified and the resulting fractions and individual compds. were identified by ir spectroscopy and gas-liquid chromatog. The compn. of the pyrolysis products is tabulated and some ir spectra and curves of gas evolution are presented. The addn. of CCl<sub>3</sub> groups to coal influences the  $\sigma, \pi$ -conjugation much more than telomerization or reactions in polychloroalkanes. The dehydrochlorination and isomerization proceeded chiefly in the coal macromols. and were dependent on the  $\sigma, \pi$ -conjugations, temp., and hindrances in the nucleophilic addn. to coal. The process is of cryptoradical, unbranched-chain type (Razuvaev, CA 58: 4587d). Formation of volatile matter is controllable by inhibitors of chain propagation so as to increase the yields to 30-100 times of those in the coking process. The pyrolysis products were more homogeneous than those from coking and contained chiefly polychloroalkanes. They were similar to the products of C<sub>2</sub>H<sub>4</sub> telomerization in the presence of CCl<sub>4</sub> or CHCl<sub>3</sub>, but contained compds. with both even and odd nos. of C atoms.

## 1966

6.41 Molten zinc halide catalysts for hydrocracking coal extract and coal. Clyde W. Zielke, Robert T. Struck, James M. Evans, Charles P. Costanza, and Everett Gorin (Res. Div., Consolidated Coal Co., Library, Pa.). Ind. Eng. Chem., Process Design Develop. 5(2), 158-64 (1966) (Eng). By using large amts.

of the catalyst, single-stage conversion of either coal ext. or coal to high-octane gasoline under relatively mild operating conditions is made possible. The more important variables of the system based on batch autoclave data are surveyed. The Zn halide and contact catalyst system are compared under equiv. operating conditions by using a com. hydrofining-type catalyst. Some of the reactions between the catalyst and the N, O, and S impurities in the coal are discussed.

#### 1961

6.42 Liquefaction of coal. Martin B. Neuworth and Leslie A. Heredy (to Consolidation Coal Co.). U.S. 3,158,561 (Cl. 208-8), Nov. 24, 1964, Appl. Dec. 22, 1961; 2 pp. A phenolic  $\text{BF}_3$  complex (I) is used for the recovery of liquid constituents from coal. I not only dissolves sol. coal constituents, but also reacts chem. with coal to depolymerize it, thus forming addnl. components which are sol. in I. The reaction is carried out at 50-200° and autogenous pressures by using a solvent: coal ratio of 0.25:1-10:1 in any conventional extn. process.

#### 1924

6.43 Distilling oils with volatile catalysts. A. M. McAfee. U. S. 1,578,049, March 23, '24. Gas oil or other oils of relatively high b.p. are heated together with  $\text{AlCl}_3$  or a similar catalyst and vapors of lower boiling oils are led away and condensed after bringing them into intimate contact with added petroleum hydrocarbon oil. U. S. 1,578,050 specifies distg. petroleum oils with  $\text{AlCl}_3$ , partially cooling the vapors to condense out  $\text{AlCl}_3$  and kerosene, separately condensing and collecting hydrocarbons of lower b.p. than kerosene, sepg. the  $\text{AlCl}_3$  from the kerosene by settling and returning the  $\text{AlCl}_3$  to the still. U.S. 1,578,051 specifies distg. oils with  $\text{AlCl}_3$  and maintaining a flow of oil through a succession of stills. Volatilized and condensed  $\text{AlCl}_3$  is returned toward the first still of the series.

#### 1921

6.44 Producing low-boiling hydrocarbons. C. M. Alexander and G. H. Taber, Jr. U.S. 1,381,098, June 14, 1921. Hydrocarbons of high b.p. such as gas oil, fuel oil or coal tar distillates of high b.p. are converted into products of lower b.p. by heating their vapors with vapors of  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , or  $\text{ZnCl}_2$ .



1918

6.45 Purifying petroleum oils with aluminum chloride. A. McD. McAfee. U. S., 1,277,329, Aug. 27, 1918. In obtaining a medicinal oil from crude asphaltic petroleum oil containing naphthenes, the oil is treated with once-used  $\text{AlCl}_3$  from a later operation until a portion but not all of the oil has been removed as low-boiling products, the  $\text{AlCl}_3$  is removed and a distd. fraction of the oil which has been thus treated is further treated with fresh  $\text{AlCl}_3$  at a temp. of about  $65^\circ$  to effect further purification without forming additional light hydrocarbons. After removing the  $\text{AlCl}_3$  for use in the first stage of the process, the oil is further refined with  $\text{H}_2\text{SO}_4$ , steamed and filtered.

1917

6.46 Cracking petroleum oils. A. M. McAfee. U.S. 1,235,523, July 31, 1917. A body of petroleum oil is heated in a still to about  $260^\circ$  with finely divided metallic Al while a current of Cl is led into the oil. Hydrocarbons produced, of low b.p., are continuously distd. off and fresh crude oil is added to maintain the volume of oil in the still constant.