

7. CO Reactions

A. CO_x + Coal

1973

7.1 138602q Hydrogenation processing of liquid coking products. Bocharov, Yu. N.; Kambarov, Yu. G.; Krichko, A. A.; Privalov, V. E.; Skvortsov, D. V.; Shustikov, V. I. (Vses. Nauchno-Issled. Inst. Olefinov, Baku, USSR). Khim. Tverd. Topl. 1973, (1), 153-4 (Russ). Optimum results were obtained with crude benzene and benzene, toluene, xylene fractions at 550-80° and 50 atm (f. p. of final benzene 5.45-5.49°, S < 0.0001%), with naphthalene oil at 520-50° (the yield of naphthalene increased by 5-10% in comparison with its content in the crude oil, f. p. 79.9-80.0°, S < 0.001%). Hydrogenation of liq. coking products yielded mainly benzene, naphthalene, and hydrocarbons C₁₋₄ at 625-50°. The yield of benzene and naphthalene increased by 10-15% in comparison with their content in raw material. Addn. of water gas (10-20% of raw material) to the reaction zone of high-temp. hydrogenation decreased the formation of coke and increased the life of the catalyst.

1972

7.2 142167y Gasification kinetics of coke with mixtures of carbon monoxide and carbon dioxide. Ulrich, K. H. (Krupp Forschungsinst., Fried Krupp G.m.b.H., Essen, Ger.). Tech. Mitt. Krupp, Forschungsber. 1972, 30(1), 49-54 (Ger). Four coke types were gasified at 900, 1000, and 1100° in the presence of CO₂-CO-N mixts. of various compns. Single test samples (5-8g) were used and reaction rates detd. gravimetrically. Gasification mechanisms are discussed.

1971

7.3 17355u Synthetic natural gas and hydrogen from the gasification of carbonaceous materials. Leas, Lawrence E.; Leas, Robert L.; Johnson, Cecil J. (Leas Brothers Development Corp.). U.S. 3,753,671 (Cl. 48/210; C 10j), 21 Aug 1973, Appl. 161,196, 09 Jul 1971; 6 pp. Synthetic natural gas is produced by first producing CO₂ by reacting CO with Co oxide, reacting the CO₂ with C in a hot bed of carbonaceous material to produce a CO-rich gas, reacting part of the CO with steam in the presence of a catalyst to produce H₂, and reacting addnl., CO with the H to produce a high-CH₄ gas. The CO is desulfurized before H prodn. by reaction of S in the gas with Co oxide, forming Co sulfide and alternately oxidizing it with air to produce SO₂. In an air-burn cycle, excess air is introduced

into the 1st bed of Co oxide to form its higher oxide after having been reduced by introduction of CO, heating the air, and introducing it into the carbonaceous bed to burn it at a higher temp. For example, char contg. C 75.9, H 1.6, S 3.2, O 0.1, N 1.4, and ash 17.8 wt.% was partially burned with air, increasing the bed temp. to 2300°F. The air flow was stopped and CO₂ was injected at 1925°F. The gasifier was maintained at 300 psia. The exit gases were filtered, cooled to 500°F, and desulfurized with Co oxide. After desulfurization, the av. gas compn. was CO 76.9, CO₂ 16.6, CH₄ 0.9, N 0.3, and H 5.3 mole %. The desulfurized gases (av. flow rate 3.25 lb/hr) were injected into a H generator contr. a Cu-Zn-Cr oxide catalyst. Steam at 500°F was injected at 1.21 lb/hr into the generator along with the gas mixt. The exit gases were dried and the CO₂ was removed. The gases were then heated to 700°F and injected into a methanization app. contg. an Fe catalyst and maintained at 700-20°F and 290-300 psia. The gas produced contained H 1.4, CH₄ 43.2, CO 3.2, CO₂ 46.8, H₂O 2.1, N 0.4, and heavier hydrocarbons (mainly C₂H₆) 2.9 mole %. After drying and removing the CO₂, a gas with a calorific value of 975 Btu/ft³ was obtained.

7.4 74573e Reduction of subbituminous coal and lignite using carbon monoxide. York, Wayne J. (Montana State Univ., Bozeman, Mont.). 1971, 166 pp. (Eng). Avail. Univ. Microfilms, Ann Arbor, Mich., Order No. 71-28,876. From Diss. Abstr. Int. B 1971, 32(5), 3685.

1970

7.5 6402q High-BTU gas from coal. Johnson, Cecil J. (Total Energy Corp.) U.S. 3,692,506 (Cl. 48-210; C 10jk), 19 Sep 1972, Appl. 11,151, 13 Feb 1970; 4 pp. High-CH₄-content gas (I) is produced by treating C and CO₂ at 2100°F in a 1st gasifier to produce CO. The gasifier is maintained at 2000°F and 100 psia. The CO is passed to a H generator having 1st and 2nd stages, and is treated with steam at 1000°F and 90 psia in the 1st stage and 450°F and 90 psia in the 2nd stage to produce H and CO₂. The CO₂ is sepd. from the H, reheated, and recycled to the gasifier for the production of addnl. CO. The H is heated to 950°F and treated with C in a 2nd gasifier at 1200°F and 470 psia to produce I. The I is cleaned to remove CO₂, H₂S, and any other impurities.

7.6 115862u Gasifier and desulfurizer for carbonaceous materials. Leas, Lawrence E.; Leas, Robert L.; Johnson, Cecil J. S. African 71 00,186 26 Aug 1971, US Appl. 2,452, 12 Jan 1970; 11 pp. Co oxide and similar reactive oxides are used for gasifying and desulfurizing carbonaceous materials

with the use of air as the regenerative fluid. Superheated CO_2 is generated which in turn converts C to CO. The higher oxide of Co reacts with the S gases in the char gasifying cycle to form Co_3S_4 . Air then regenerates the Co. The S gases are absorbed in an alc. recovery unit. Co_3O_4 is arranged in a 1st bed, clean coke in a 2nd bed, and Co_3O_4 in a 3rd bed in series flow whereby CO is oxidized to CO_2 in the Co beds and the coke is gasified with the superheated CO_2 to CO. As the air is regenerating the S-bearing bed, it is also reheating the coke bed and the CO_2 in the top Co bed. Excess heat is used to generate steam and electricity. Ash is removed as a sep. product. Just enough regeneration air is used to release the S from Co_3S_4 to facilitate the more complete recovery of the S.

7.7 47316e Reactivity of anthracite and various cokes. Akhmetov, S. A.; Khaibullin, A. A. (Ufim. Neft. Inst., Ufa, USSR). Khim. Tverd. Topl. 1970, (3), 82-91 (Russ). A method for investigating the reactivity of carbonaceous materials with H_2O is based on the direct detn. of one of the components and the vol. of the products of reaction in the course of the whole expt. The kinetic equations proposed for the reaction $\text{C} + \text{CO}_2$ were applicable to the reaction $\text{C} + \text{H}_2\text{O}$. The reaction capacities of five petroleum cokes, three metallurgical cokes, pitch coke, and anthracite with H_2O were detd. at 850-1160°, by measuring the concn. of CO_2 with an automatic opticsacoustic gas analyzer, and the total vol. of gaseous products. The rate of reaction $\text{C} + \text{H}_2\text{O}$, as for $\text{C} + \text{CO}_2$, was 1st order. The ratio of the apparent reaction rate consts. depended on the temp. of reaction, the degree of gasification of the carbonaceous material, and its properties. The values and sign of the coeff. characterizing the rate of change of the apparent reaction rate const. with consumption of carbonaceous materials was detd. by the nature of the carbonaceous material, and the gasifying agent. The apparent energies E of activation for reactions $\text{C} + \text{H}_2\text{O}$ and $\text{C} + \text{CO}_2$ were 36-62 kcal/mole, and the values $E_{\text{H}_2\text{O}}/E_{\text{CO}_2}$ of cokes and anthracite were 0.77-1.2.

1969

7.8 45845g Solubilization of low rank coal with carbon monoxide and water. Appell, H. R.; Wender, I.; Miller, Richard Dennis (Pittsburgh Coal Res. Center, Bur. of Mines, Pittsburgh, Pa.). Chem. Ind. (London) 1969, 47, 1703 (Eng). Minus 100-mesh coal was treated at pressures near 4500 psi in a 500-ml autoclave. The residue was then extd. with C_6H_6 , giving a yield of 80-95% of the conversion.

7.9 115861t Gasifying carbonaceous materials to a carbon monoxide fuel gas product. Johnson, Cecil J. (Total Energy Corp.) U.S. 3,635,672 (Cl. 23/204M; C 01b, C 10b), 18 Jan 1972, Appl. 810,101, 25 Mar 1969; 6 pp. S-contg. carbonaceous material is gasified to produce CO which is desulfurized and then used as heat energy for mech. or elec. power in internal combustion engines, gas turbines, chem. processes, and steam boilers. Since the CO has been desulfurized, a min. of pollutants is added to the atm.; e.g., carbonaceous material, e.g., coal, coal char, petroleum coke, or a mixt. of coal tar and petroleum coke, is gasified by passing a main flow of superheated CO₂ through >1 bed of carbonaceous materials in which the CO₂ reacts with the C to form CO, creating >1 vapor zone in the bed. The main stream of CO₂ is supplemented with O to the vapor zones for selective reaction with CO simultaneous to the CO₂-C reaction to produce addnl. hot CO₂, whereby addnl. heat and CO₂ is supplied in the vapor zone for endothermic reaction of CO₂ gas and C.

1964

7.10 Effect of carbon monoxide on the reduction of carbon dioxide by carbon of solid fuels. A. D. Kokurin and D. A. Rozental. Tr. Leningr. Tekhnol. Inst. im. Lensovet No. 63, 148-52 (1964) (Russ). Redn. of CO₂ was studied by method described by K. and R. (CA 57, 16977a) at 900, 1000, and 1100° by using 30, 50, and 100% CO₂ in CO gas mixts. blown through coke layers of various thicknesses and 5-7 mm. particle size. At 900°, the CO₂ reactivity was very low and independent of the thickness of the coke layer and of the concn. of CO₂. At 1000-1100°, anal. of CO₂ was markedly inhibited by a high concn. of CO₂ formed during the redn. This temp. corresponded to the max. of chemisorption of CO by the C of the exptl. fuel. Active CO formed during the reaction inhibited CO₂ redn. more than the blown-in CO.

7.11 Effect of structure of a fuel on the reduction of carbon dioxide. A. D. Kokurin and D. A. Rozental. Tr. Leningr. Tekhnol. Inst. im. Lensovet No. 63, 144-7 (1964) (Russ). The redn. capacity of a fuel depends on the surface area. The surface area of electrode coke and anthracite was increased 2.5-3 times by oxidn. of their powders at 300-400° for 6-8 hrs.

7.12 Aspects of the reactivity of porous carbons with carbon dioxide. John H. Black (Univ. of Colorado, Boulder), Gordon B. Bopp, John F. Jones, Mathew G. Miller, and William Tambo. Am. Chem. Soc., Div. Fuel Chem., Preprints 8(1), 247-62 (1964) (Eng). The reaction at 900° of CO₂ with porous, calcined, subbituminous coal particles was followed by suspending the sample from a balance. Since a 5-fold range of

particle sizes had no effect on the rate, diffusion did not appear to be controlling. For samples stabilized by thermal treatment, the reaction rate was practically const. until as much as 55% of the C was consumed. During reaction, the surface area nearly trebled and reached a max. at ~35% burnoff. Thus, the pore surface had no effect on the rate. Regeneration of a reactive site each time a C atom leaves the solid state as CO is believed to cause the const. reaction rate.

1963

7.13 Reaction of carbon dioxide with Karan anthracites at temperatures of 850° to 1100°. Tae Hee Hahn (Seoul Natl. Univ., Korea). Daehan Hwahak Hwoejee 7(4), 288-92 (1963). The rates of reaction of various Korean anthracites with CO₂ were measured at temps. from 850° to 1100° with coal of 6-8 mesh temps. and temps. residence time of reactant gas in the fixed coal bed 14.0 to 15.0 sec. The reactivity varied considerably with the coal sources and increased sharply with increase in reaction temp. except for Yongwol coal where the increase was not so sharp, which is due to high reactivity and the high-pore structure of the coal. A straight line was obtained when a logarithm of the rate consts. is plotted against the reciprocal of the abs. temp. up to 1000°; but above that temp., it deviates from linearity. The information obtained will be of value in the design of a coal gasifier using Korean anthracites.

1962

7.14 Gasification of coal. Eugene J. Burban. Fr. Addn. 83,253 (Cl. C 10j), July 17, 1964, Appl. Aug. 28, 1962; 3 pp. Addn. to Fr. 1,298,850 (CA 59, 7273c). In the generation of CO, CaCO₃ is used to react with the C according to the equation $\text{CaCO}_3 + \text{C} = \text{CaO} + 2\text{CO}$.

7.15 Gasification of solid fuels in a slagging producer. Finacalor A.-G. (by Zsigmond de Galocsy). Brit. 1,024,341 (Cl. C 10j), March 30, 1966, Appl. Jan. 18, 1962; 3 pp. In a gas producer in which molten slag is sprayed into a furnace as the principal heat source, use of O or highly enriched air preheated to $\geq 1000^\circ$ as the gasification agent allows the use of low-grade coal or coke as fuel. When the gasification agent contains CO₂ and/or H₂O, the following reactions occur: (1) $2\text{C} + \text{O}_2 = 2\text{CO}$; (2) $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$; (3) $\text{C} + \text{CO}_2 = 2\text{CO}$. As reaction (1) is exothermic and (2) and (3) are endothermic, (1) predominates. The H reacts with S in the fuel to produce H₂S, and ores blown into the furnace are reduced.

1954

7.16 Carbon monoxide almost free from carbon dioxide by gasification of coke with oxygen. Dr. C. Otto and Co. G.m.b.H. and Sueddeutsche Kalkstickstoff-Werke A.-G. (by Erich H. Becker-Boost and Hermann Kronacher). Ger. 1,146,221 (Cl. 24e), Mar. 28, 1963, Appl. Dec. 17, 1954; 5 pp. Dry O is blown through jets into the bottom of a water-cooled gas generator (inside diam.-to-height ratio 1:2) filled with dry coke of 20-40 mm. size at a velocity of 100-150 m./sec. and a pressure sufficient to extend the 1600° gasification zone close to the surface of the coke. Part of the CO thus produced is cooled and recirculated through similar jets surrounding the O jets to cool the coke outside the gasification zone below 600°. By thus restricting the temp. range to 600-1600°, a gas contg. 97-99 vol. % CO is produced.

B. Modified Fischer-Tropsch

1972

7.17 37375s Coal refinery. Tangible concept. Egbal, J.; Sarkar, S. (Dep. Chem. Eng., Indian Inst. Technol., Bombay, India). Petrol. Hydrocarbons 1972, 7(1), 1-9 (Eng). Pub. in Chem. Age India, 23(4). A review with 21 refs. The hydrogenation of coal, coal tar, and coal extracts and the technically sound but economically impractical Fischer-Tropsch gasification of coal are discussed. A proposal is discussed for the conversion of Assam coal into oil by direct hydrogenation and for establishing a combined refinery in which half the plant capacity will be met by the oil from conversion of coal (syncrude) and the other half by natural crude.

7.18 5625u Gasoline via the Fischer-Tropsch reaction using the hot-gas recycle system. Elliott, J. J.; Haynes, W. P.; Forney, A. J. (Bur. Mines, Pittsburgh, Pa.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1972. 16(1), 44-50 (Eng). A test run was conducted in the hot-gas recycle pilot plant. Heat of reaction is removed by recycling relatively large amts. of reacted gas. The catalyst was a raw magnetite ore that was flame sprayed onto sheet steel assemblies, thus achieving a catalyst form with a very low resistance to gas flow. The yield of C₁ and C₂ gases was high, generally 30-40% of the hydrocarbons formed. The remainder of the hydrocarbons ranged up to heavy waxes and were comparable to products obtained with other forms of Fe catalyst. The gasoline yield approached 60% of the hydrocarbon prodn.

1967

7.19 134921w Direct conversion of carbonaceous material to hydrocarbons. Hoffman, Edward J. (University of Wyoming) U.S. 3,505,204 (Cl. 203-10, C 10g), 07 Apr 1970, Appl. 10 Apr 1967; 7 pp. A method is described for converting carbonaceous material directly to hydrocarbons and O-contg. org. compds. Steam reacts at 800-1200°F with carbonaceous material in a 2-component catalyst system. The 1st is an alkali metal or alk. earth compd. and the 2nd is a Group VIII transition metal compd.

1965

7.20 Hydrogenation of carbon monoxide and carbon dioxide on supported ruthenium catalysts at moderate pressures. F. S. Karn, J. F. Shultz, and R. B. Anderson (U.S. Dept. of the Interior, Pittsburgh, Pa.). Ind. Eng. Chem., Prod. Res. Develop. 4(4), 265-9 (1965) (Eng). Ru-on-Al₂O₃ catalysts contg. 0.5 wt. % Ru are effective catalysts for hydrogenation of CO and CO₂. The mol. wt. of the product decreases sharply with increasing H/CO ratio of the feed gas. Large yields of hard wax were produced with H₂ + CO mixts. at 21.4 atm. and 220°. CH₄ was the principal product with 4H₂ + CO₂. With 3H₂ + CO, the rate increased with total pressure to the 1.2 power.

1964

7.21 Hydrogen sulfide poisoning of nitrided and carbided iron catalysts in the Fischer-Tropsch synthesis. F. S. Karm, J. F. Shultz, R. E. Kelley, and R. B. Anderson (U.S. Dept. of the Interior, Pittsburgh, Pa.). Ind. Eng. Chem., Prod. Res. Develop. 3(1), 33-8 (1964). S poisoning of Fe Fisher-Tropsch catalysts was investigated because synthesis gas prepd. by gasification of coal contains S compds. The poisoning of fused Fe oxide catalysts converted to Hagg carbide by H₂S in 1H + 1CO feed gas was quite similar to the poisoning of the corresponding reduced catalyst; however, the carbided catalyst required about twice as much S as the reduced sample for poisoning to the same extent. For catalysts converted to ε-Fe nitride, the activity decreased less rapidly with S fed to the catalyst than with reduced or carbided catalysts. When the temp. was increased to compensate for loss in activity, moderately long tests at const. productivity were possible. Catalysts used in tests in which operating temps. were >300° were less oxidized than the same catalysts in synthesis tests at 250° to 260°. In the high-temp. poisoning tests, nitrided catalysts were partly converted to Hagg carbide.

7.22 Development of catalysts and reactor systems for methanation. J. H. Field, J. J. Demeter, A. J. Forney, and D. Bienstock (U.S. Dept. of the Interior, Pittsburgh, Pa.). Ind. Eng. Chem., Prod. Res. Develop. 3(2), 150-3 (1964). A hot gas-recycle reactor and a tube-wall reactor were effective for catalytic conversion of synthesis gas to CH_4 . Partially reacted synthesis gas contg. an appreciable concn. of CH_4 can also be treated in these reactors to increase the heating value to over 900 B.t.u./ft.³ Raney Ni sprayed onto plates is used as the catalyst in the hot gas reactor, while in the tube wall the catalyst is applied to the wall. Excellent heat removal and temp. control have been experienced with both reactors. The hot gas-recycle system has been developed to a larger scale than the tube-wall reactor, but efforts are now being directed to the latter because it offers possible elimination of all or most gas recycle and decreased power on consumption. One vessel serves as reactor and waste heat recovery unit.

7.23 The design and operation of a pilot-scale plant for hydrocarbon synthesis in the slurry phase. R. Farley and D. J. Ray (D.S.I.R., Warren Springs Lab., Stevenage, Engl.). J. Inst. Petrol. 50 (482), 27-46 (1964). The Fischer-Tropsch process for the production of gaseous, liquid, and solid hydrocarbons from CO and H was studied in a liquid-phase (slurry) pilot plant. The synthesis gas used (H:CO ratio 0.7:1) was of the type produced in complete coal gasification. A period of ~3 years is covered, with 14 runs. The solids/liquid sepn. system developed for this process is described, and typical data for the synthesis and for heat and mass transfer are given. Gas hold-up in the reactor was measured during synthesis; this fell with increasing viscosity of the slurry associated with the formation of finely divided C. The reactor could be operated for 400-500-hr. periods at an hourly space velocity of 200 (based on expanded slurry vol.) and at a gas conversion of 50%, maintained by increases in temp. from 260 to 280°. At the higher temps., the C build-up was such that the increase in viscosity ultimately led to gelation of the reactor contents. The best performance achieved (50-60% conversion at a space velocity of 200) compares unfavorably with that obtainable in the 1st stage of a modern fixed-bed reactor when using synthesis gas of H:CO ratio of 1.2:1.

7.24 Kinetics of the Fischer-Tropsch synthesis on iron catalysts. R. B. Anderson, F. S. Karn, and J. F. Schultz (U.S. Bur. of Mines, Pittsburgh, Pa.). U.S. Bur. Mines, Bull. 614(7) 45 pp. (1964). Nitrided Fe catalysts were studied at 21.4 atm. with feed gases having a H:CO molar ratio of 0.25-2:1, and at 7.8-21.4 atm. with a feed gas of 1:1 H:CO molar ratio. The activation energy increased with increasing CO content of the

feed gas from 19.5 kcal./mole for a 2:1 H:CO to 23.7 gas kcal./mole for a 0.7:1 H:CO gas. The rate of synthesis with a 1:1 H:CO gas increased linearly with operating pressure from 7.8 to 21.4 atm. In other expts., H₂O, CO₂, Ar, and CH₄ were added to a 1:1 H:CO feed gas and a nitrated catalyst. Important factors of catalyst geometry in detg. the synthesis rate were particle size and extent of redn. Expts. carried out at 21.4-103 atm. are also described.

7.25 Experiments with a self-generated, carbon-expanded iron catalyst for the synthesis of methane. J. J. Demeter, W. P. Haynes, and A. J. Youngblood (U.S. Bur. of Mines, Pittsburgh, Pa.). U. S., Bur. Mines, Rept. Invest. 6425(4), 37 pp. (1964). The synthesis of high B.t.u. gas, using the Fischer-Tropsch reaction, was studied in a 2-in.-steel tube-wall reactor. The catalyst (I) was C-expanded Fe, formed on the walls of a steel reactor exposed to a synthesis gas of H and CO in 1:1 ratio. I did not operate effectively under the test conditions. After a coating had built up to <0.1 in., it would flake off. The thick layers of I resulted in poor temp. control and high operating temps. Tests in fixed, packed beds suggest that the most likely application for the I in producing high B.t.u. gas would be a moving bed reactor, where bed movement and heat removal are provided to prevent plugging.

7.26 Effects of additions of propylene and 1-butene on formation of hydrocarbons of low molecular weight under Fischer-Tropsch synthesis conditions. Atsushi Nakai and Shigeru Saito (Hosei Univ., Tokyo). Nippon Kagaku Zasshi 85(6), 354-8 (1964). Effects of addns. of propylene (7.1-11.8 vol. %) and a 1-butene (8.2-9.2 vol. %) to water gas (H₂/CO 2:1) in the Fischer-Tropsch reaction were studied at 165-200° under atm. pressure over a Co catalyst with reactant space velocity of 50 and 100 vols./vol./hr. The product analysis was limited to C₁₋₄ hydrocarbons. Addn. of propylene or 1-butene increased the vol. shrinkage and the % CO change. The addn., in general, did not suppress the abnormal reaction of water gas and increased the formation of CO₂ and CH₄. Addn. of propylene increased C₂H₆ formation. This may be due to hydrocracking of C₃H₆:
 $C_3H_6 + H_2 \rightarrow C_3H_8$, $C_3H_6 \rightarrow CH_4 + C_2H_4$, $C_2H_4 + H_2 \rightarrow C_2H_6$. At >180°, the added propylene was completely hydrogenated and an appreciable amt. of C₄H₁₀ forms. Addn. of 1-butene suddenly increased C₂H₆ formation at 175°. C₂H₆ may be formed by the same mechanism as C₂H₄ above. 1-Butene not only was hydrogenated, but also was isomerized to trans-2- and cis-2-butene, with the former in larger amt. At 250°, 1-butene and isobutenes were almost completely hydrogenated except for a small amt. of trans-2-butene.

1963

7.27 Fischer-Tropsch synthesis. Poisoning of iron catalysts by H_2S in synthesis gas. F. S. Karn, J. F. Shultz, R. E. Kelly, and R. B. Anderson (U.S. Dept. of the Interior, Pittsburgh, Pa.). Ind. Eng. Chem., Prod. Res. Develop. 2, 43-7 (1963). The poisoning of Fe Fischer-Tropsch catalysts by small concentrations of H_2S in synthesis gas was studied. Reduced, fused Fe oxide and reduced steel turning catalysts were tested with synthesis gas containing 6.9, 23, and 69 mg. of S as H_2S per cu. meter, at 260° . For both catalysts, the activity decreased linearly with the amt. of S fed to the catalyst until about 60% of the activity was lost and 0.2 to 0.3 mg. S per g. of Fe had been introduced. On further poisoning, the activity decreased less rapidly with S introduced. The activity of the turnings decreased steadily to 0 when 1 to 2 mg. S per g. Fe was introduced; however, the activity of the fused Fe oxide catalysts approached a const. value of 5 to 10%. By increasing the temp., the productivity of fused Fe oxide catalysts could be maintained const. for moderate periods of time.

7.28 Pipeline gas from coal by methanation of synthesis gas. H. A. Dirksen and H. R. Linden (Inst. of Gas Technol., Chicago). Inst. Gas Technol., Res. Bull. No. 31, 137 pp. (1963) (Eng). Catalytic methanation of synthesis gas was extensively studied in fixed and fluidized-bed lab. and pilot-plant reactors. Over 90% $H + CO$ conversion to CH_4 was maintained for extended periods at operating conditions of 30-300 psig. and $600-900^\circ F$. The most active catalysts were Ni-on-kieselguhr and a novel Raney Ni catalyst made by caustic leaching of a 42% Ni-58% Al alloy. These catalysts are poisoned by S compds. In lab. tests, total conversion capacities of $20-40 \times 10^3$ ft.³ CH_4 per lb. of original alloy were obtained with Raney Ni catalyst at 75-150 psig., a space velocity of 10,000 ft.³ gas/ft.³ catalyst/hr., and a 3:1 mole ratio of $H:CO$, in the feed gas. These high conversion capacities were not observed in fluidized-bed pilot plant equipment; the difference is attributed to backmixing in the bed. A description of exptl. equipment, Raney Ni catalyst prepn., discussion of the theory of performance of this catalyst in fluidized beds, and tabulation of exptl. data are given. 105 references.

7.29 Performance of slurry reactor for Fischer-Tropsch and related syntheses. A. K. Mitra and A. N. Roy (Indian Inst. Technol., Kharagpur). Indian Chem. Engr. 5(3), 127-32 (1963). The slurry reactor was 2 in. in diam. and 10 ft. high. The catalyst was pptd. Fe and the synthesis gas was a 1.33:1 ratio of H to CO. The activity of the catalyst was linear with pressure at 100-50 lb./sq. in. gage. The usage ratio was const. at $240-60^\circ$ but showed an increasing trend with pressure. At 260° , 150 lb./sq. in. gage, and an hourly space velocity of

100, 94% of the CO was converted, the usage ratio was 1.24, and a yield of 174 g. of liquid products/m.³ of CO plus H was obtained. The yield of CH₄ was 1.5-6 g./m.³ CO plus H. Daniel Bienstock.

7.30 The action of alkali promoters upon iron catalyst. VI. Influence of potassium carbonate upon selectivity. 1. Herbert Koelbel and Horst Giehling (Tech. Univ., Berlin). Brennstoff-Chem. 44(11), 343-7 (1963); cf. CA 60, 7498f. The conversion efficiency of Fe catalysts in the production of hydrocarbons from CO and H reaches a max. at 0.2 part K₂CO₃/100 parts Fe and falls off rapidly at higher alkali content. Catalyst performance is related to surface area, pore vol., av. pore radius, d., C content, and preparative method. The surface area is only slightly affected by K₂CO₃ content in the reduced or annealed catalyst, but it reaches a max. at 0.3% in the dried material. The av. pore radius changes only very slightly at K₂CO₃ concns. <0.1%, but the product distribution is shifted rather strongly to higher mol. wts. and olefin contents. In comparison, between 0.6% and 1.0% K₂CO₃ there is a parallel relation between av. pore radius and the proportion of higher-boiling paraffin product.

7.31 Reaction mechanisms of the Fischer-Tropsch synthesis. VIII. Formation of methane during hydrogenation-cracking. Herbert Koelbel, Hans Bolko Ludwig, and Hans Hammer (Tech. Univ., Berlin). Brennstoff-Chem. 44, No. 3, 87-90 (1963); cf. CA 57, 9266h. CH₄ formation in the Fischer-Tropsch process was studied. Use was made of C¹⁴ compds. over Co, Fe, and Ni catalysts under appropriate conditions. At normal pressure and temp., only 5% of the primary contact paraffin consists of CH₄ formed by catalytic cracking. In the case of Fe catalysts, the value is 3%. Elevation of the temp. to 204° increases CH₄ formation when Ni catalysts are used. The crit. temp. is 213° in the case of Co catalysts. Cf. ibid. 35, 161 (1954), CA 45, 2177a.

7.32 Carbides, nitrides, and carbonitrides of iron as catalysts in the Fischer-Tropsch synthesis. J. F. Schultz, L. J. E. Hofer, K. C. Stein, and R. B. Anderson (U.S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Bull. No. 612, 70 pp. (1963). Haegg carbide, hexagonal carbide, and cementite are considered. Reduced, fused-Fe catalysts, converted to Haegg Fe carbide by treatment with either CO or a 1:4 H:CO mixt. and converted to cementite by direct carburization or by thermal reaction of Haegg Fe carbide and Fe, were tested in the Fischer-Tropsch synthesis with gas at 7.8 to 21.4 atm. Phase changes in the catalysts were detd. by thermomagnetic analysis and x-ray diffraction. Synthesis tests were made on catalysts converted to nitrides and carbonitrides.

1962

7.33 Fischer-Tropsch synthesis. Prepoisoning of iron catalysts by sulfur compounds. J. F. Shultz, L. J. E. Hofer, F. S. Karn, and R. B. Anderson (Bur. of Mines, Pittsburgh, Pa.). J. Phys. Chem. 66, 501-6 (1962). The poisoning of iron catalysts by S compounds in the Fischer-Tropsch synthesis was investigated, since synthesis gas obtained by the gasification of coal contains H_2S and other S compds. The pretreated catalysts were prepoisoned by immersion in a soln. of the S compd. in C_7H_8 prior to synthesis. SO_2 was the most severe poison, and H_2S and EtSH were nearly as effective. Results of tests of reduced catalysts poisoned by COS and CS_2 , as well as a nitrided catalyst poisoned by H_2S , were erratic. However, for all S compds. tested, the activity of a reduced fused Fe oxide catalyst (I) was decreased to <2% of the value for the fresh sample by addn. of about 10 mg. S/g. Fe or 0.7 mg. S/sq.in. of surface. Activated steel turnings were more susceptible to S poisoning than the I. S poisonings decreased the av. mol. wt. of the synthesis products and increased the $H_2:CO$ usage ratio. These changes in selectivity suggest that the poison may in part react with the alkali promoter.

1961

7.34 The conversion of South African low-grade coal to oil and chemicals. P. E. Rousseau. Trans. Commonwealth Mining Met. Congr. 1, 375-93 (1961). Oil fractions ranging from motor fuel to heavy fuel oil are made from coal by use of the Fischer-Tropsch synthesis at Sasolburg. The process is inefficient in C utilization: for every 100 lb. of C charged to the gasification, 20 lb. of C is found in the synthesis products. Large supplies of low-cost coal are therefore essential.

7.35 Coal gas as a substitute for synthesis gas in the Fischer-Tropsch synthesis. IV. Variations of reaction characteristics with time. G. C. Basak and N. C. Niyogi. J. Technol., Bengal Eng. Coll. 6, No. 1, 49-60 (1961); cf. CA 57, 1207b. Calcutta city gas was allowed to react over a Co catalyst at 180° and a space velocity of 100 vols./vol./hr. for 4 100-hr. reaction periods, with catalyst regeneration between periods with H at 400° and 3000 vols./vol./hr. space velocity. Hydrocarbon production increased from 42.2 g./cu. m. in the 1st period to 60.5 g./cu. m. in the 4th period. Catalyst activity decreased rapidly, with hydrocarbon production being maintained for only the first 24 hrs. of the exptl. period. Activity loss appeared to be due to oxidn., as evidenced by H_2O formation during regeneration.

1960

7.36 Coal gas as a substitute for synthesis gas in Fischer-Tropsch reactions. III. G. C. Basak and N. C. Nyogi (Bengal Eng. Coll., Howrah, India). J. Technol., Bengal Eng. Coll. 5, 117-26 (1960); cf. CA 55, 8318b. The types of reactions involved and the nature of the products formed in the synthesis reaction at 180, 190, and 200° were studied. Coal gas (typical analysis CO₂ 5.38, H 25.9, O 2.7, CH₄ 19.05, unsatd. hydrocarbons 3.10, C₂ and higher satd. hydrocarbons 0.41, CO 7.25, and N 36.23%) reacted over a catalyst (MgO-ThO₂-kieselguhr) at a rate of 100 cu. m. of gas/cu. m. of catalyst/hr. The gas was purified to remove O and S compds. The only hydrocarbon formed initially was CH₄. After about 6 hrs., CH₄ formation virtually ceased and formation of higher hydrocarbons increased. The overall conversion efficiency decreased from about 80% to <50% in the 100-hr. test period.

7.37 Synthesis of high-B.t.u. gas from carbon monoxide and hydrogen using a hot-gas-recycle reactor. D. Bienstock, J. H. Field, A. J. Forney, and H. E. Benson (U.S. Bur. of Mines, Pittsburgh, Pa.). Proc., Operating Sect., Amer. Gas Assoc., CEP-60-14, 9 pp. (1960). Catalytic methanation of a mixt. of 2.5-3 parts H and 1 part CO over a steel catalyst (prepd. from lathe turnings by oxidn. with steam) followed by treatment over Raney Ni in a hot-gas-recycle system was studied. Thus, 99% of H + CO was converted to a gas of 983-1130 B.t.u./ft.³ and contg. 78-96% CH₄ and no CO. With steel catalyst, conversion was only 85-90%, and the heating value of the product gas was 810-868 B.t.u./ft.³

1959

7.38 Study of gasification of solid fuels by the isotope tracer method. I. G. Petrenko. Trudy Inst. Goryuchikh Iskopaemykh, Akad. Nauk S.S.S.R. 11, 9-22 (1969). Investigation by tracer methods indicates that the interaction of oxides of C with C proceeds with formation of 3 compds. on the surface of coal: (1) cyclic oxycarbon compds. followed by decompn. with formation of elementary C followed by evolution of CO (a heterogeneous C exchange reaction); (2) primary straight-chain compds. of oxycarbon followed by decompn. and formation of CO₂ (in the reverse direction, the reaction is the basis of 3 processes. heterogeneous reactions with exchange between CO and CO₂, velocity redn. with regeneration of CO₂ in the oxidn. of C, and oxidn. of C); (3) secondary straight-chain oxycarbon compds. of the carbonyl type as a result of decompn. of primary compds. with simultaneous formation of CO and C, or due to instantaneous interaction of O₂ with coal. The oxidn. of CO proceeds easily in the presence of solid fuel. This explains

the formation on the coal surface of oxides of the carbonyl type which interact easily with CO and appear to be the reason for the decrease in the reaction regenerating CO₂ and stepping up of the oxidn. of CO.

C. Gasification

1. Catalytic

1973

7.39 Catalysis of coal gasification at elevated pressures. W. P. Haynes, S. J. Gasior, and A. J. Forney (Bur. Mines), 165th ACS Natl. Meet. (Dallas 4/8-12/73) ACS Div. Fuel Chem. Prepr. 18, No. 2:1-28 (1973). Screening tests on 19 g samples of a high-volatile bituminous coal plus 0.5 g of catalyst, conducted by the U. S. Bureau of Mines, were made at 850°C, 300 psig, and 5.8 g/hr. of steam carried by 2000 cu cm/hr of nitrogen. All of the 35 additives tested, including Raney nickel, and iron, bismuth, boron, lead, copper, and zinc oxides, increased the total gasification rate and the yields of desirable gases (methane, hydrogen, carbon monoxide). The effects of temperature, steam rate, gasification time, and method of catalyst admixture were investigated. Potassium salts in ash residues from total coal gasification still retained most of the activity for producing methane, lost part of ability to increase hydrogen production, but inhibited carbon monoxide production. Pilot-plant trials adding lime or dolomite at 5% concentration to coal fed to a 4 in. dia. Synthane gasifier system resulted in significant increases in yields of methane, hydrogen, and carbon monoxide. Tables.

7.40 Liquid feed offers quick way to SNG. Anton Roeger III (Texas Eastern Transmission Corp., Shreveport, La.). The Oil and Gas Journal, 25 June 1973.

7.41 Study of active sites on MRG catalyst by means of pulse technique. Akjo Okagami et al. (Japan Gasoline Company, Yokohama, Japan). Division of Petroleum Chemistry, ACS Dallas Meeting, Apr. 8-13, 1973.

7.42 SNG catalyst technology. J. T. Richardson, Hydrocarbon Processing, Dec. 1973, 91-95.

1972

7.43 Future catalytic requirements for synthetic energy fuels. G. A. Mills. ACS, 1972.

7.44 The poisoning of a steam hydrocarbon gasification catalyst. F. Moseley, R. W. Stephens, K. D. Stewart, J. Wood (The Gas Council, Midlands Research Station, Wharf Lane, Solihull, Warwickshire, Eng.) Received Sept. 22, 1970. Journal of Catalysis 24, 18-39 (1972). The factors which affect the loss of activity of a nickel alumina catalyst for the gasification of sulfur-free light hydrocarbons with steam at temperatures below 500°C have been examined. These are sintering or loss of active surface area due to heat treatment in steam, and poisoning of active sites by a much slower parallel reaction to gasification involving constituents of the hydrocarbon feedstock. The second of these modes of activity loss is much more important at temperatures between 400 and 500°C and normal operating pressures around 25 atm. This second mode of poisoning is independent of total pressure but rises rapidly with the boiling point of the hydrocarbon feedstock and the hydrocarbon steam ratio supplied. Increases in temperature favor the gasification reaction at the expense of poisoning. With finely divided catalyst particles, the rate of the gasification reaction is chemically controlled and zero order with respect to steam and hydrocarbon. With larger particles (0.3 cm diam), the rate is controlled by gaseous diffusion in the pores of the catalyst and, in line with this, the reaction rate becomes proportional to the particle size, the reaction order rises, and the activation energy falls. Rate control is probably by Knudsen diffusion in the micropores, though bulk diffusion in the macropores cannot be ruled out. The poisoning rate falls sharply at first on entering the region of diffusional control as the particle diameter is increased, but ultimately becomes independent of size. An attempt is made to interpret this phenomenon in terms of the effects of diffusional rate control on steam hydrocarbon ratio and temperature.

1971

7.45 61663j Hydrogasification of brown coal to produce methane natural gas. Birch, T. J. (Aust.). Aust. Chem. Process. Eng. 1971, 24 (10), 29-36 (Eng). The process was tested in 3 stages: one with a cocurrent 3-ft. fluidized bed, a 2nd with a counter-current 19-ft. bed, and a 3rd with 2 cocurrent 3- and 15-ft. beds in series. All were elec. heated and run continuously at 500-1200° with 5-36 lb/hr Victorian brown coal in 3-in.-diam. Inconel tubes within cooled pressure vessels at 500-600 psi (15-600 psi of H in N). In the 3rd stage, the short 1st reactor controlled the initial fast reaction with the volatile matter and discharged the further-reducible char to the 15-ft. reactor, where cooling coils (N) and cocurrent operation kept the exothermic mixts. below 900°.

The 850° max. conversion to CH₄ vs. theory was 8 ft³/20.5 ft³, consuming 13 ft³/38 ft³ of H per lb of dry ash-free coal and leaving some N and S in the char. The rate consts. at 850° were 7.6 X 10⁻³ lb/atm-lb of bed C for the volatile matter and 5.4 X 10⁻³ lb/atm-lb for the residual C. The heat of reaction was 65 Btu/ft³ H consumed. Up to 234 ft³ of CH₄/hr was produced, yields decreasing with increasing time and temp. up to 900°. The thermal efficiencies were 99 and 95% at 47 and 65% coal conversion, resp. Important variables were the bed d. ρ and ρv^2 , in which v is the gas surface velocity. Pneumatic transportation of solids and sepn. of the 2 reactions are suggested.

1970

7.46 102438c Coal and char transformation in hydrogasification of coals ranging in rank from lignite to low-volatile bituminous. Mason, David McArthur (Inst. of Gas. Technol., Chicago, Ill.). Ind. Eng. Chem., Process Des. Develop. 1970, 9(2), 298-303 (Eng). The effect of rank on the behavior of coal at different stages in hydrogasification was examd. petrographically. Among 5 high-volatile bituminous coals, the yield of coal from the pretreatment increased slightly with rank. Structure and anisotropy of the hydrogasification residues indicated that the higher the rank of the coal, the greater the fluidity in the interior of the particles when they were rapidly heated in the reactor. Escape of this material from inside the pretreatment skin caused agglomeration when a low-volatile bituminous coal was processed. Lignite and subbituminous coals, run without pretreatment, gave residue chars with a lenticular pore structure. In some regions of these residue chars, the presence of rounded pores indicated the development of a degree of plasticity.

1969

7.47 41103a Hydrogenation of coal to give methane-containing gases. Dent, Frederick J.; Thompson, Brian Hoyle; Conway, Henry L. (Gas Council) Brit. 1,154,322 (Cl. C 10b), 04 Jun 1969, Appl. 06 Oct 1966; 5 pp. Coal is hydrogenated to provide a CH₄-contg. gas in a fluidized bed of noncaking material at 600-1000° under 10-200 atm. in the presence of a hydrogenating gas. The hydrogenation gives gaseous hydrocarbons which arise mainly from the volatile constituents of the coal, esp. at the lower temps., and give a residue of noncaking powd. char. This char may be hydrogenated under more severe conditions in a later stage of the process to produce more CH₄ and also a residue which may be used for manuf. of H. The use of a fluidized bed facilitates temp. control of the

reactions which are exothermic. The temp. of the process is controlled by the preheat temp. of the reactants and by the controlled oxidn. of part of the fluidized bed. The noncaking material in the fluidized bed can be the noncaking char produced by the hydrogenation of the powd. raw coal, and the introduction of the coal and the extn. of the treated char are both operated continuously. Details of the app. and the operating techniques have been described previously (Brit. 1,154,321) except that a liq. hydrocarbon feedstock was used in place of raw coal.

7.48 (New catalytic concepts for the) conversion of coal to gasoline. G. A. Mills. I. Engr. Chem., July 1969, 6-17.

1966

7.49 22658n Production of carbon monoxide and hydrogen from solid carbonaceous fuels. Baron, Gerhard; Kapp, Ernst; Dernbach, Heribert; Bieger, Franz; Kohlen, Rudolf (Metallgesellschaft A.-G. and Ruhrgas A.-G.) U.S. 3,540,867 (Cl. 48-197; C 10jk), 17 Nov 1970, Ger. (East) Appl. M 69,561, 20 May 1966; 8 pp. Gases from the pyrolysis of solid carbonaceous fuels are cooled to 180° to remove the dust and the condensible materials. O and CO₂ are added and the gas stream is passed over a ceramic cleaving catalyst at 700°. The cleaved gases are cooled to condense H₂O and are scrubbed to remove CO₂, NH₃, and S compds. The cleaving catalyst is supported on Al₂O₃ or MgO and contains a metal, oxide, or sulfide selected from an element of Group VI or VIII of the periodic table.

1962

7.50 Hydrogasification of bituminous coals, lignite, anthracite, and char. Raymond W. Hiteshue, Sam Friedman, and Robert Madden (U.S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 6125, 15 pp. (1962). To aid in designing a continuous system for evaluating processes for converting coal to high-B.t.u. gas, the Bureau detd. the amenability of various coals and a char to hydrogasification at 800° and 6000 lb./sq. in. gage by using a Mo catalyst. A lignite from Rockdale, Texas, an hvCb coal from Rock Springs, Wyoming, a char from the low-temp. carbonization of the latter, an hvAb coal from Pittsburgh, and an anthracite from Luzerne County, Pa. were tested. The highest yields of gaseous hydrocarbons, 94%, were produced from char, and the lowest yields, 67%, were obtained from lignite. Hydrocarbon bases contained

CH₄ 82-92, C₂H₆ 8-15, and C₃H₈ 1-3%. More oil was produced from lignite than from the bituminous coals. Oils boiled below 300° and contained less than 4% asphaltenes. No oils were produced from char or anthracite. Small yields of coronene, a polynuclear compd., were obtained by hydrogenating anthracite.

C. Gasification

2. Selected Processes

General surveys
Bi-Gas
CO₂ Acceptor
COED
FMC
Hydrane
Hygas
Kellogg
Koppers-Totzek
Lurgi, Pressure Gasification
Slagging
Westinghouse
Producer
Other

1973

7.51 21455y Coal gasification. COED process plus char gasification. Shearer, H. A. (American Oil Co., Whiting, Ind.). Chem. Eng. Progr. 1973, 69(3), 43-9 (Eng). A conceptual design was given for a plant to produce 250 X 10⁶ std. ft³/day of pipeline gas and ~27,000 bbl. of synthetic crude oil/stream day from coal. The plant utilizes the COED coal pyrolysis process along with a molten salt process to gasify COED char. The COED process is based on multistage fluidized bed pyrolysis of coal to produce oil, gas, and char. Approx. half of the charge is converted to char. A molten salt process is used to gasify the char and to produce high-Btu pipeline gas from the combined COED and gasification gases.

7.52 21453w Kellogg's coal gasification process. Cover, A. E.; Schreiner, W. C.; Skaperdas, G. T. (M. W. Kellogg Co., Houston, Tex.). Chem. Eng. Progr. 1973, 69(3), 31-6 (Eng). The gasification of coal in a bath of molten Na₂CO₃ through which steam is passed is the basis of the Kellogg coal gasification process. The original 2-vessel gasification system with a gasifier and combustor was changed to a single-vessel system because of the endothermic reaction of steam with Na₂CO₃ ($\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$) at 1800°F. The molten bath

can handle caking coal directly, the molten carbonate has a strong catalytic action, and at the uniform high temp. all tar components are gasified to maximize the gas yield and eliminate some pollution control facilities. The catalytic action permits gasification at lower temps. to maximize CH_4 formation during gasification and decrease O consumption.

7.53 161929k Coal gasification. Low Btu for power station emission control. Agosta, J.; Illian, H. F.; Lundberg, R. M.; Tranby, O. G. (Commonw. Edison Co., Chicago, Ill.). Chem. Eng. Progr. 1973, 69(3), 65-6 (Eng). Addnl. data considered in abstracting and indexing are available from a source cited in the original document. A clean fuel is obtained by the pressure gasification of coal with air and steam. Tars and liq. hydrocarbons are recirculated and all ash is removed. The gas is desulfurized and expanded through a turbine. The low-Btu gas exiting from the gas turbine is sent to a steam-turbine plant for addnl. elec. generation. The efficiency of the gasification plant is 80%.

7.54 21454x Coal gasification. Evaluating the bi-gas SNG process. Hegarty, W. P.; Moody, B. E. (Air Prod. Chem., Inc., Allentown, Pa.). Chem. Eng. Progr. 1973, 69(3), 37-42 (Eng). The Bi-Gas process of the Bituminous Coal Research, Inc., for the prodn. of synthetic natural gas is theoretically sound. Potential problems of the gasifier are considered and the shift conversion, air sepn., acid gas removal, S recovery, and methanation and drying are discussed.

7.55 21459c Coal gasification. Two-stage coal combustion process. Karnavas, J. A.; LaRosa, P. J.; Pelczarski, E. A. (App. Technol. Corp., Pittsburgh, Pa.). Chem. Eng. Progr. 1973, 69(3), 54-5 (Eng). Addnl. data considered in abstracting and indexing are available from a source cited in the original document. The 2-stage coal combustion process consists of dissolving coal in a mass of molten iron where the coal-fixed C and S are retained, and the coal volatiles cracked and emitted in the off gas as CO and H. The dissolved C in the iron is gasified by reaction with combustion air to yield addnl. CO to the off gas. The dissolved S migrates to a lime-bearing slag floating on the molten iron to form CaS. An essentially SO_2 -free off gas for subsequent combustion in a power plant boiler is produced via the molten iron gasification method. The process can be used to gasify coal for elec. power plants without SO_2 emission into the atm.

7.56 106678y Supplemental pipeline gas from coal by the hydrane process. Feldmann, Herman F.; Wen, Chin Vung; Simons, William H.; Yavorsky, Paul M. (Pittsburgh Energy Res. Cent., Bur. Mines, Pittsburgh, Pa.). AIChE Symp. Ser. 1973, 69(127), 74-6 (Eng). Addnl. data considered in abstracting

and indexing are available from a source cited in the original document. A process is described for direct conversion of coal with H to give CH_4 . The operating conditions are 1100 psi of H flowing upward through a free-falling pulverized coal at 725°. The coal must fall freely for 15 ft. to prevent agglomeration before being concd. for the high-temp. reaction. CO_2 , H_2S and dust are then removed from the product.

7.57 39112q HYGAS process. Schora, Frank, Jr.; Lee, Bernard S.; Huebler, Jack (Inst. Gas Technol., Chicago, Ill.). World Gas Conf., (Proc.), 12th 1973 (Pub. 1973). IGU/B 3-73, 20 pp. (Eng). Int. Gas Union: London, Engl. Status of the coal gasification process development on a pilot-plant scale is described. Possibility of the generation of high-heating-value gas (by HYGAS process) suitable for injection into pipeline systems is discussed.

1972

7.58 87013p Development of the HYGAS process for converting coal to synthetic pipeline gas. Lee, B. S. (Inst. Gas Technol., USA). J. Petrol. Technol. 1972, 24(Dec.), 1407-10 (Eng). The coal is crushed, ground, and sized and if it is an agglomerating type it is treated to destroy the agglomerating properties. To attain a pressure of 1000 psi in the hydrogasifier, a coal-oil slurry is used (the oil is a by-product of the process and is recovered for recycling). Hydrogasification is done in 2 stages: at 1300-1500°F to produce CH_4 in a high yield from the volatile matter, then at 1700-1800°F to produce CH_4 and to effect the steam-coal reaction to generate H. The other half is used to generate H. The hot raw gas from the gasifier dries the incoming slurry by evapn. the carrier oil, and then is quenched to recover the oil and condense unreacted steam. Gas purifn. follows to remove CO_2 , S compds., etc. Complete S removal is necessary to prevent contamination of the Ni-base catalyst later. Purified feed gas for methanation contains CH_4 60, CO 10, and H 30%. The CO and H react over the catalyst to form CH_4 at 550-850°F. This temp. is controlled by recycling cold product gas. The final product contains 95% CH_4 and <0.1% CO (the rest is H and inerts), has a heating capacity of 950 Btu/ft³, and is fully interchangeable with natural gas.

7.59 21452v Low-sulfur char as a co-product in coal gasification. Curran, G. P.; Clark, William Edgar; Pell, Melvyn; Gorin, Everett (Res. Div., Consol. Coal Co., Library, Pa.). U. S. Nat. Tech. Inform. Serv., PB Rep. 1972, No. 214162/0, 70 pp. (Eng). Avail. NTIS. From Govt. Rept. Announce. (U.S.) 1973, 73(5), 174-5. The prodn. of low-S char as a co-product with low-S producer gas in a gasification-desulfurization process with bituminous coal was studied.

CaCO₃ was used as a S acceptor. Preoxidized coals were extremely responsive to desulfurization. Chars were obtained contg. $\leq 0.5\%$ S. Low-S char was produced at a lower Btu cost than was the case for complete gasification to low-S producer gas.

7.60 39141y Two-stage gasification of pretreated coal. Donath, Ernest E. (Bituminous Coal Research, Inc.). Ger. Offen. 2,312,350 (Cl. C 10b), 11 Oct 1973, U.S. Appl. 237,332, 23 Mar 1972; 29 pp. A process for producing CH₄ comprises 2 stages. In the 1st stage, fine particulate coal and steam are reacted at 1370° and 50 atm to give H-rich synthesis gas. Methanization occurs in the 2nd stage, when partially carbonized coal and synthesis gas react in a gasification zone at 870° and at ≥ 50 atm pressure. A part of the semicarbonized coal is recycled to the 1st stage of make synthesis gas. Fuel gas of $\geq 70\%$ CH₄ is obtained as final product.

7.61 29134j Two-stage coal gasification with forced mixing. Donath, Ernest E. (Bituminous Coal Research, Inc.). Ger. Offen. 2,312,283 (Cl. C 10b), 11 Oct 1973, U.S. Appl. 237,360, 23 Mar 1972; 18 pp. In the manuf. of CH₄-enriched fuel gas by reaction of charred material from the 2nd stage with O and steam in a 1st stage to give synthesis gas and reaction of this gas in the 2nd stage with coal and steam to give the charred material and a product gas contg. CH₄, H, and C oxides, the synthesis gas was passed through a mixing zone of reduced diam. into the 2nd stage. The temps., pressures, gas velocities, and residence times of the solids were adjusted such that the reactants flowed upward in whirls to give quick gasification at a temp. above the m.p. of the slag formed in the 1st stage and above the region of coal plastification in the 2nd stage. The product gas was purified and methanized to give a fuel gas contg. >70 vol. % CH₄.

7.62 5636y Gasifying coal in several fluidized-bed compartments. Archer, David H.; Brecher, Lee E. (Westinghouse Electric Corp.) Ger. Offen. 2,262,971 (Cl. C 01j). 19 Jul 1973, U. S. Appl. 216,950, 11 Jan 1972; 18 pp. Pulverized coal mixed with CaO is dried in the 1st fluidized bed by the gas from the 2nd bed. The coal is devolatilized and desulfurized in the 2nd bed by the gas from the 3rd bed and the CaO, and CaS is discharged from the bottom of the 2nd bed. In the 3rd bed, the devolatilized coal is partially gasified by the gas from the 4th bed. The partially gasified coal is completely gasified in the 4th bed by air and steam. The gas from the 2nd bed is the product. A 5-bed system is described for a power plant with a gas turbine, a steam generator, and a steam turbine.

7.63 5622r Hydrogenated COED oil. Johns, John H.; Jones, John F.; McMunn, Bert D. (J. J. Johns Assoc., Villanova, Pa.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1972, 16(1), 26-35 (Eng). The COED process converts coal by fluidized-bed pyrolysis into gas, oil, and char. A catalytic hydrogenation pilot plant was constructed to hydrogenate oil produced in the COED process from coal. Desulfurization, denitrification, and deoxygenation of this plant was compared with previous hydrogenation studies. The properties of the gasoline, middle distillate, gas oil, and bottoms produced were defined in petroleum refining terms.

7.64 142151p Coal desulfurization aspects of the Hygas process. Feldkirchner, H. L.; Schora, F. C., Jr. (Inst. Gas Technol., Chicago, Ill.). Air Pollut. Contr. Off. (U.S.) Publ. 1972, AP-109, III-2, 9 pp. (Eng). The steps involved in the Hygas process for desulfurization of coal are discussed: (1) coal pretreatment, (2) hydrogasification, and (3) electrothermal gasification.

7.65 51059y Gasification of lignites in a fluidized bed under pressure using air-water blowing. Sechenov, G. P. (Inst. Goryuch. Iskop., Moscow, USSR). Khim. Tverd. Topl. 1972, (3), 96-102 (Russ). An air-water mixt. can be used instead of steam to produce water gas from a fine-grain lignite in a fluidized bed at 0.5-20 atm. This decreases the consumption of water and energy and the cost of steam production equipment. The water is converted into steam, is superheated in the oxidn. zone of the fluidized bed, and has no effect on the gas formation process in the redn. zone. Depending on the compn. of the initial air-water mixt., water gas can be obtained which has the same compn. and energy value as gas obtained with steam.

7.66 167010e New horizons for pressure gasification. Production of clean energy. Hebden, D.; Percival, G. (Res. Dev. Div., Gas Counc., London, Engl.). Inst. Gas Eng., J. 1972, 12(8), 229-44 (Eng). A review is given of processes for converting fossil fuel feedstocks into CH₄ for com. distribution under development by the Gas Council; coal hydrogenation, catalytic CH₄ synthesis, fluidized-bed oil hydrogenation, gas-recycle oil hydrogenation, catalytic rich-gas process, and slagging coal gasification. No refs.

7.67 142135m Syngas from coal. Schora, Frank C., Jr. (Inst. Gas Technol., Chicago, Ill.). Proc., Annu. Conv., Natur. Gas Process. Ass., Tech. Pap. 1972, 51, 114-18 (Eng). The CSG, BI-GAS, Synthane, and IGT HYGAS processes, and the Lurgi gasifier, are reviewed briefly. No refs.

1971

7.68 161948r Coal gasification. Donath, Ernest E. (Bituminous Coal Research, Inc.) Ger. Offen. 2,245,735 (Cl. C 10j), 29 Mar 1973, U.S. Appl. 182,652, 22 Sep 1971; 25 pp. Gas contg. 94.8% CH₄ and solid fuel contg. 0.72% S of high calorific value were manufd. by 2-step gasification of coal. In the 2nd step, the gasification of coal with superheated steam (540°) and product gas of step 1 at 72 atm and 925° gave a gas mixt. contg. 38.7% CO and 17.3% CH₄ and solid char. In the 1st step, gasification of a part of this char with superheated O (425°) and steam at 72 atm gave C oxides and H. The other part of the char was used as fuel for the steam generation. Thus, this 2-step gasification of coal contg. C 74.7, H 5.0, N 1.5, S 3.8, and O 7.8% gave a char contg. 0.72% S and a gas contg. CO₂ 15.9, CO 38.7, CH₄ 17.3, H₂ 26.0, N 0.7, and H₂S 1.4%. This gas was passed through a water-gas reactor for CO conversion to give after removal of H₂S and CO₂ a gas contg. CH₄ 94.8, CO₂ 1.14, CO 0.06, H 2.0, and N 2.0%.

7.69 6401p Gasification of crude lignite. Schenck, Hermann; Wenzel, Werner (Rheinische Braunkohlenwerke A.-G.) Ger. Offen. 2,212,880 (Cl. C 10b), 28 Sep 1972, Australian Appl. 26,877/71, 23 Mar 1971; 22 pp. Crude lignite was gasified by passing through a tubular, slightly inclined, and indirectly heated chamber whereby the water content of the coal was used as the gasification agent. The coal was transported by changing the pressure of the developed gases and vapors by automatic valves.

7.70 100293b Synthesis gas. Seglin, Leonard; Eddinger, Ralph Tracy (FMC Corp.) Ger. Offen. 2,204,990 (Cl. C 01j), 24 Aug 1972, U.S. Appl. 114,642, 11 Feb 1971; 14 pp. Synthesis gas manufd. from coal and steam in a fluidized-bed gasifier, is passed into a cyclone sepg. system and the finest suspended solids thus sepd. are burned in a combustion chamber with preheated air. The hot combustion gas is passed into a heater contg. a swirling bed of heat resistant pebbles which are carried by the gas stream into the gasifier above the fluidized bed. Thus, make-up char and recirculated pebbles are combined in the gasifier with steam at 871° and 2.45 atm. The heavy pebbles sink to the bottom of the fluidized bed and are recirculated to the heater. The fine suspended solids sepd. in the cyclone are burned with preheated air at 282° and heat the pebbles in the heater to 1038°. The hot gases from the heater are freed from the ash and are passed at 1038° and 2.45 atm through a waste heat burner, a gas turbine, and finally through an air preheater.

7.71 161930d Kellogg coal gasification process. Cover, A. E.; Schreiner, W. C.; Skaperdas, G. T. (M. W. Kellogg Co., Houston, Tex.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1971, 15(3), 1-11 (Eng). The Kellogg Coal Gasification Process conducts the gasification reaction in the presence of a molten salt that serves as a heat-transfer medium and as a catalyst for coal gasification and hydrogenation reactions. In the latest version of this process, gasification is carried out with steam at 1200 psi and heat is supplied by circulating molten salt from a sep. combustion vessel wherein C in the melt is burned with O. These conditions were chosen to maximize CH₄ prodn. in the gasifier which, in turn, minimizes O consumption and subsequent gas processing costs. An alternate version of the process features elimination of the sep. combustor by injection of the O into the gasifier.

7.72 161931e Status and design characteristics of the BCR/OCR bi-gas pilot plant. Farnsworth, J. F.; Glenn, R. A. (Koppers Co., Inc., Pittsburgh, Pa.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1971, 15(3), 12-31 (Eng). The planning for a multipurpose research pilot plant facility for manufg. pipeline-quality gas from coal featuring a 5 ton/hr BI-GAS pilot plant as the initial installation is outlined. Design characteristics of the unit operations involved are presented and discussed.

7.73 161932f Basic features of the carbon dioxide acceptor gasification process. Mosher, D. R.; Marwig, U. D.; Phinney, J. A. (Stearns-Roger Corp., Rapid City, S. Dak.). Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1971, 15(3), 40-51 (Eng). An OCR pilot plant which embodies the essential features of the CO₂ Acceptor (Consol. CSG) gasification process is described. The unique gasification and heat supply concepts are reviewed. The solids handling systems and gas clean-up systems incorporated in the pilot plant are discussed.

7.74 161933g Strongly caking coal gasified in a stirred-bed producer. Lewis, Paul S.; Liberatore, A. J.; McGee, J. P. (Bur. Mines, Morgantown, W. Va.). American Chem. Soc., Div. Fuel Chem., Prepr. 1971, 15(3), 52-61 (Eng). An exptl. gasifier of fixed-bed design is described and operating data are shown for the conversion of strongly caking coal into fuel gas for power generation or industrial heating. Agglomerated fuel that forms masses of cohesive coke and stops the fuel flow is broken up by continuous stirring of the bed. Fixed-bed gas producers have used noncaking coal heretofore in order to avoid agglomeration. Nuclear gages indicate bed level and gross variations in d. within the bed. Operating data at >80 psig are discussed for feeds of high-volatile A and B bituminous coals from Pittsburgh and Illinois No. 6 beds.

7.75 22641b Electrothermal coal char gasification. Kavlick, V. J.; Lee, B. S.; Schora, F. C. (Inst. Gas Technol., Chicago, Ill.). AIChE Symp. Ser. 1971, 67(116), 228-35 (Eng). In a 300-kW electrothermal gasification pilot unit, a high-temp. high-pressure synthesis gas was manufd. by the steam gasification of coal char. The product was a feed gas for the Hygas conversion of coal to pipeline gas. In tests at 1000 psig, 1690-900°F, char residence times 6-12 min, and power levels >10 kW, criteria were sought necessary for the design of a 2-MW electrothermal gasifier for integration into a Hygas pilot plant.

7.76 55733c Energy-producing gas from fine-grained coal. Sechenov, G. P.; Leonova, L. D.; Larin, L. I. (Institute of Mineral Fuels) U.S.S.R. 372,247 (Cl. C 10j), 01 Mar 1973, Appl. 26 Jul 1971. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1973, 50(13), 79. The gasification of fine-grained coal in a fluidized-bed app. with an inert substrate at >2 atm. absolute with the use of a steam-air blast and a fluidized bed is changed to increase the heat of combustion by passing part of the gasification product through the upper part of the fluidized bed, mixing the produced gas components at the app. outlet with the common gas stream, and directing the unreacted powdered carbon forming during gasification and heat treatment and the resin vapors to the moving bed of inert substrate. Water atomized by air is fed to the lower oxidn. zone of the fluidized bed.

1970

7.77 7772t City gas from coal by self-ignition in a generator. Dubovy, Ervin Czech. 146,810 (Cl. F 23r), 15 Jan 1973. Appl. 5946-70, 31 Aug 1970; 2 pp. To start the process, a gas generator is charged with the coal, sealed, and the pressure increased to 30 atm with superheated steam. After reaching the self-ignition temp., air is fed until the CO₂ content in the effluent gas increases to >20% and the O content decreases to <1% and the temp. in the upper part of the regenerator is 120-140°. The generator is ready for gas prodn. after supplying coal and feeding O. A sorption app. for measuring the equil. sorption isotherm and the rate of diffusion of CH₄ from fine-sized coal was designed and constructed. With Pittsburgh and Pocahontas No. 3 coal, the diffusion coeff. varies with pressure and the fracture spacing in these 2 coals is substantially different.

7.78 142166x Gas for gas turbines by Lurgi pressure gasification of coal. Rudolph, P. (Lurgi Ges. Waerme-und Chemotech. m.b.H., Frankfurt/M., Ger.). Technology 1970, 7 (No. 4) (Spec. Iss.), 112-15 (Eng). Power generation by Lurgi

pressure gasification of coal in conjunction with gas turbines has major technol. advantages such as high gasification efficiency, less water consumption, and no by-product disposal problem. This process can compete with conventional thermal plants for power generation.

7.79 142165w Synthesis gas production by Lurgi pressure gasification of coal. Rudolph, P. (Lurgi Ges. Waerme-und Chemotech. m.b.H., Frankfurt/M., Ger.). Technology 1970, 7 (No. 4) (Spec. Iss), 116-25 (Eng). Principles of the Lurgi pressure gasification of coal for gas production are outlined. The gas from coal gasification processes after purification and conditioning can be used as synthesis gas for the production of NH_3 and MeOH by heterogeneous catalysis. A comparison is made between several process schemes for gas purification and conditioning of NH_3 synthesis gas with regard to investment cost and overall efficiency.

1969

7.80 149603s Coal gasification process and apparatus. Rheinische Braunkohlenwerke A.-G. Brit. 1,309,396 (Cl. C 10b), 07 Mar 1973, Ger. Appl. P 19 43 080.9, 25 Aug 1969; 3 pp. Pulverized, high-moisture-content coals, esp. lignite, are effectively gasified in inclined tubes; the heat for the process being provided by burning the solid gasification residue by-product. Initially, the coal is predried from 56-9% to 40% moisture, the water being removed from the system as steam; the dried coal is then fed into a gasification tube inclined at 10-30° to the horizontal where the remaining water and volatiles are expelled. The temp. is then increased to 800-900° and the steam passed over the volatile-free coal to yield a high-quality gas comprising H and CO. The calorific value of the gas produced is ~60% of that of the original coal, and the heat for the process is produced by burning the coke formed (while still hot, using preheated air). Further thermal economy is effected by heat exchange between the effluent gases and the wet coal and also the air required to burn the coke.

7.81 116642e Gasifying carbonaceous fuels in a fluidized bed. Huttner, Rudolf; Schulze-Bentrop, Roland; Teggers, Hans (Union Rheinische Braunkohlen Kraftstoff A.-G.) Brit. 1,285,654 (Cl. C 01jg), 16 Aug 1972, Ger. Appl. P 19 07 324.6, 14 Feb 1969; 6 pp. The fuels are initially degassed and largely gasified in a fluidized bed after which the gasification mixt. formed contg. low-temp. coke, tar, and gas is allowed to react to completion on further heating in a suspended bed. Some of the heat of reaction required is supplied in indirect heat exchange both in the fluidized and the suspended bed. Solid as well as liq. carbonaceous fuels may be used. The heat required

for carrying out the endothermic gasifying reaction is supplied by indirect heat exchange. Steam heated to about 1000° can be passed through suitable heat-exchange systems arranged in the fluidized bed and the suspended bed. The steam can be heated in indirect heat exchange by the hot coolant gas, such as He, from a high-temp. nuclear reactor. Hot flue gas from the combustion of low-grade coal may be used in the heat exchange system. Heat may also be transferred to the system by means of a bath of liq. metal.

1966

7.82 Lurgi-gasifier tests of Pittsburgh-bed coal. W. H. Oppelt, H. Ferry, J. L. MacPherson, and E. J. Vitt (U.S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 6721, 31 pp. (1966) (Eng). To extend the use of fixed-bed pressure gasifiers, the upper section of the gasifier top contains a rotating coal distributor and stirrer equipped with blades that cut 2 ft. below the surface through the fuel bed, breaking up any coke-agglomerates formed and permitting coking coals to be safely processed. This device, if applicable to strongly coking coals, would enhance the production of high-Btu. gas from coal in the U.S., because the coals in the Appalachian region are strongly coking. Approx. 100 tons of such coal, highly fluid, from the Arkwright mine in Osage, W. Va., was tested in Germany in a Lurgi fixed-bed gasifier. To reduce the coking potential, ash refuse from the gasification of Dorsten (Leopold) coal was added to prepare coal-ash mixts. contg. 20-30% ash. Tests were run for 4.75 and 12.5 hrs., resp. The 12.5-hr. test addn. of ash refuse to obtain 30% ash in the Arkwright coal indicated the operation to be feasible with this mixt. This coal contained H₂O 1, volatile matter 39, fixed C 53, ash 7.2, H 5.3, C 78, N 1.5, and O 5.7%. The heating value was 14,000 Btu/lb., the free-swelling index 7.5, and the agglutinating value 8.9.

7.83 92622p Coal hydrogasification. J. Huebler and F. C. Schora (Inst. of Gas Technol., Chicago). Chem. Eng. Progr. 62(2), 87-91 (1966) (Eng). A direct process is described for making high-Btu gas from coal by using 2-stage hydrogasification. In the high-temp. stage operating at 1700°F or above, the partially gasified coal from the low-temp. stage is treated with H₂O and H. An effluent CH₄ compn. of 25-30% is obtained from the C-H exothermic reaction plus H from the C-H₂O endothermic reaction. In the low-temp. hydrogasifier operating at 1200-1500°F, the fresh coal or char reacts with the CH₄-contg. gases from the high-temp. reactor. A gas of 600-800 Btu/ft.³ is obtained. To upgrade to 950-1000 Btu, the acid gases are removed to give a 3/1 H/CO ratio and the remaining gas is treated with a catalyst to form CH₄.

7.84 Balanced-pressure pilot reactors. H. A. Dirksen and B. S. Lee (Inst. of Gas Technol., Chicago). Chem. Eng. Progr. 62(6), 98-102 (1966) (Eng). The direct gasification of coal is studied in a versatile pilot-plant unit at pressures up to 2000 psig. and temps. up to 220°F. A low-temp. pressure shell encloses, but is insulated from, a reactor-heater assembly. Pressure balance is maintained between the shell and the reactor tube by a differential-pressure controller that controls the shell pressure as a slave to the reactor pressure. Gases flowing to the shell and reactor are sep., with the shell pressurized by N and the reactor by whatever gaseous reactants are being used. Insulation, heating, bed-level control, and other assocd. features are reported.

7.85 Reactivity of non-degassed coals and their function during gasification under pressure. Jiri Romovacek and Jan Malinsky (Hochsch. Chem. Technol., Prague). Brennstoff-Chem. 47(4), 114-20 (1966) (Ger). A differential method permitted measurement of the reactivity of low-temp. carbonization coke in the nascent state. The sample (1 g.) was degassed and gasified in a tube with a CO₂ stream, while another was simultaneously only degassed in a 2nd tube with N (flow rate 100 ml./min. in each case). The temp. was raised linearly (4°/min., to a max. of 1260°) in the furnace in which both tubes were located. The off-gases were catalytically burned with a fixed amt. of O in countercurrent combustion cells. The indications of a Wheatstone bridge were recorded as a function of temp. The temp. (T_R) at which 50% of the gasifiable C was converted to CO was taken as a measure of the reactivity. This value increased with the coalification (from Sardice lignite to Vitezny "unor" coked coal), and depended on the O consumption ($Y = -848 + 1.19T_R$, where Y = O consumption in m.³/ton pure coal) in the Lurgi gasification. 27 references.

7.86 Effect of moisture in coal on its pressure gasification. K. Prasek, B. Konrad, and R. J. Riedl. Paliva 46(1), 3-7 (1966) (Czech). The effect of 13.5-37.7% by wt. H₂O was investigated in an exptl. generator 2.6 m. in diam. A decrease of 1% by wt. H₂O decreased the O consumption by 0.6%, the compn. of the gas changed only negligibly. With a min. moisture content, the output rose to 13,000 m.³/hr. without any process difficulties.

7.87 Gas generation under pressure from coal, gasoline, and natural gas. Franz Bieger (Steinkohlengas A.-G., Dorsten, Ger.). Paliva 46(7-8), 249-53 (1966) (Czech). The quantity of steam necessary for gasification was reduced and the content of CO lowered by the conversion of CO. Cracking of raw gas increased the H content. Two generators, usually used for coal, were converted into reactors for gasifying light gasoline and for converting natural gas into gas with a high H content.

7.88 The production of city gas from solid and liquid fuels. Paul F. H. Rudolph (Lurgi Ges. Waermetech. m.b.H., Frankfurt, Ger.). Paliva 46(7-8), 262-7 (1966) (Czech). Gasification of coal under pressure and a combination of this with gasification of liquid hydrocarbons, or with carburetion of H-rich gas from natural gas, were studied. The conversion of CO and cracking of hydrocarbons in crude gas were also studied. Pressure gasification with the Shell process of oil gasification and the production of H-rich gas and NH_3 were investigated.

7.89 Theory of pressure gasification of lignitic tar by using partial oxidation. E. Rammler and P. Goehler (Deut. Brennstoff-Inst., Freiberg, Ger.). Paliva 46(7-8), 290-6 (1966) (Czech). It is indicated that complete gasification of lignite with O is not economically practical. Therefore, partial oxidn. is feasible, the final products being mainly oils and water gas. The utilization of oils is manifold, e.g., in the Shell Process. Variables such as pressure, temp., and material compn. are mentioned, tabulated, and graphically illustrated. Also, processes for city gas, enriched city gas, and city gas and NH_3 are dealt with.

7.90 Manufacture of liquid products in the Schwarze Pump combine. Heinz Schaedlich. Paliva 46(7-8), 296-9 (1966) (Czech). Various techniques of pressure coal gasification and utilization of various gaseous and liquefied products are described.

7.91 Fluidized bed under pressure as a method for transformation of fuels. G. P. Sechenov and V. S. Al'tshuler. Teoriya i Tekhnol. Protsessov Pererabotki Topliva, Inst. Goryuch. Iskop. 1966, 82-93 (Russ). Use of a fluidized bed under pressure in thermal and thermocatalytic transformation of fuels was studied. Brown coal, dimensions 0-10 mm., was subjected to gasification at 20 atm. gage to give 10,000-12,000 kg./m.²/hr. A highly productive process of steam-O conversion of hydrocarbon gases in a fluidized bed at 10,000-15,000 hrs.⁻¹ space velocity, 3-4 $\text{H}_2\text{O}-\text{CH}_4$ ratio, 900-300°, and 20 atm. gage is described, which gave synthesis gas and H with 97-8% conversion. The method can be used in coking, enriching of coal, and contact coking of heavy fuels.

7.92 Production of synthesis gas from high ash noncoking coals in an experimental fixed-bed slagging gasifier. P. Kameswara Rao, P. P. S. Sarma, K. Seshagiri Rao, and M. Ramacharyulu (Regional Res. Lab., Hyderabad). Chem. Age India 17 (3), 185-92 (1966) (Eng). The current status of research in slagging gasification of low-grade, high-ash coal with O and steam for the production of synthesis gas is reviewed. An atm. fixed-bed slagging gasifier was developed in which semicoke obtained from low-temp. carbonization of high-ash (30%) noncoking

coals of the Singareni coal fields having a H:C ratio of $\sim 0.4:1$ was gasified by using blast-furnace gas and dolomite as flux, yielding synthesis gas contg. 30% CO + H. An O-steam mole ratio of 1.12-1.27:1 was used, depending on the ash content of the fuel. The results show that the operation is successful if the gasification is carried out under pressure. Performance data of the exptl. high-pressure slagging generator are compared with a water gas generator, high-pressure Lurgi generator and Grand Forks (North Dakota) slagging generator and show better or comparable efficiencies. The gasifier performance became more reliable with increase in throughput. Nitrite-bonded SiC brick was the best refractory.

7.93 Coal gasification approaches pilot-plant stage. Anon. Chem. Eng. News 44(16), 68-73 (1966) (Eng). A survey and description of 4 processes which promise to be competitive with natural gas by the early 1970's. The processes are: (1) the hydrogasification process, an offspring of Gas Technology in Chicago; (2) Consolidated Coal's CO₂ acceptor process; (3) M. W. Kellogg's molten salt process; and (4) Bituminous Coal Research's 2-stage superpressure entrained gasification process.

1965

7.94 Reaction of coal with steam-hydrogen mixtures at high temperatures and pressures. H. L. Feldkirchner and Jack Juebler (Inst. Gas Technol., Chicago). Ind. Eng. Chem., Process Design Develop. 4(2), 134-42 (1965) (Eng). The rate of hydrogasification of low-temp. bituminous coal char with steam, H, and steam-H mixts. was measured at conditions not previously studied in a novel, rapid-charge, semiflow reactor system. Rates were measured at 1000 psig. and 1700-2100°F under conditions of very rapid coal heatup and very short exit gas residence times. The primary variables studied were temp., degree of C gasification, and feed gas-steam-H ratio. Data were obtained for use in designing reactors for high-pressure, high-temp. steam-H gasification of low-temp. bituminous coal char.

1964

7.95 The CO₂ acceptor gasification process. G. P. Curran and Everett Gorin (Res. Div., Consolidation Coal Co., Library, Pa.). Am. Chem. Soc., Div. Fuel Chem., Preprints 8(1), 128-46 (1964) (Eng). The CO₂-acceptor process is briefly described. The process produces an H-rich gas from carbonaceous fuels without the use of O. The heart of the process is the steam bearing acceptor. The acceptor serves the purpose of providing the endothermic heat of the gasification process by

absorption of CO_2 to produce CaCO_3 . Simultaneously, gas purification to produce an H-rich gas is effected. The CaCO_3 is continuously calcined by air combustion of the ungasified fuel in a fluidized-bed regenerator. The limiting conditions under which the process can operate, as detd. by the properties of the acceptor, are defined. The acceptor must show a high rate of absorption of CO_2 under process conditions, must be phys. rugged, and must be resistant to chem. deactivation under the conditions imposed in the gasification and regeneration steps. High-purity dolomites meet all the requirements of the process. Equil. values in the absorption of H_2S and CO_2 and the regeneration reactions of the corresponding Ca sulfide and CaCO_3 were detd. The impact of these equil. on the limits of operation of the process is discussed. The limits imposed by fusion of the acceptor under high steam pressures are also discussed.

7.96 Some operational results from the first plants for the conversion of hot raw gas for the gasification of coals under pressure. F. Bieger. Intern. Gas Conf., 9th, The Hague, 1964, IGU-B1-64, 14 pp. (Ger). The pressure gasification of hard coal has been further developed by Steinkohle A.-G. at Dorsten in Germany. The coal gas must be enriched by addn. of natural gas. The high steam consumption of pressure gasification and the high Cl content of the gas can be reduced by a conversion process. First, a pilot plant was designed esp. to combat corrosion problems. Later, Lurgi A.-G. built 2 com. plants for the pressure gasification of hard coal.

7.97 Hydrogasification of high-volatile A bituminous coal. Raymond W. Hiteshue, Sam Friedman, and Robert Madden (U. S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. No. 6376(3), 31 pp. (1964); cf. CA 58, 5418h. Expts. were made in a semicontinuous unit. At 800° and with a coal residence time of several sec., yields of hydrocarbon gases increased from 2000 s.c.f. (standard cu. ft.)/ton at 250 psig /lb./in.² gage) to 7000 s.c.f. at 1000 psig. With 15 min. residence time, yields from 800 s.c.f./ton at 250 psig to 17,500 cu. ft. at 100 psig. Small amts. of heavy oils were produced along with the gaseous hydrocarbons in all cases but were minimized by increasing the retention time of the volatiles in the hot zone. Yields of gaseous hydrocarbons from char were slightly greater than from coal under similar conditions. Although the hydrogasification reaction is very pressure-dependent, 40-60% of the coal could be converted to gaseous hydrocarbons at pressures as low as 50 psig provided reaction temps. were increased to 1200° . The above coal could be hydrogasified continuously without incurring agglomeration by dispersing the coal in a large reactor with concurrent flow of H. At 1000 psig and 800° , about 35% of the coal was converted and produced a gas contg. up to 52% CH_4 .

7.98 Pressure carbonization of a high-volatile A bituminous coal to produce high-Btu gas. Raymond W. Hiteshue, Sam Friedman, Paul Dobransky, and Robert Madden (U. S. Bur. of Mines, Pittsburgh, Pa.). U. S. Bur. Mines, Rept. Invest. 6424(4), 20 pp. (1964). Pittsburgh-seam coal cont. moisture 1.6, volatile matter 35.9, fixed C 56.4, and ash 6.1% was carbonized in a closed system at 600° and 40-1200 lb./in.² gage to produce a high-Btu gas and char. By retaining the volatiles within the system, it was possible to eliminate production of tars and oils. Depending on pressure and residence time, yields of combustible gases (72-92% CH₄) were 4000-6000 ft.³/ton coal (moisture and ash free), and gross heating values of these gases varied from 880 to 930 Btu/ft.³ Yields of char (moisture and ash free) were about 1000 lb./ton coal (moisture and ash free). Increased residence time favored production of gases but reduced their heating values. Increase in pressure gave higher heating values and lower production. Similar effects were observed from the carbonization of a low-temp. tar. If these results could be translated to an economical carbonization process for producing high-Btu gas from coal, the demand for coal could be expanded 40-50 million tons per year. Because of large yields of char, a process of this type would have to be integrated with coal-fired power plants. Operations could be conducted near atm. pressure as product gas under these conditions can be obtained in good yields and with good quality.

7.99 The gasification of coal in an experimental Rummel double-shaft slag-bath gasifier. M. Maccormac and J. Wrobel (London Res. Sta., Gas Council). Gas Council (Gt. Brit.), Res. Commun. GC113, 14 pp. (1964). Pilot expts. were made in an Otto-Rummel gasifier on the use of molten slag, both as heat-transfer fluid and as reaction medium. Although a satisfactory diluent gas was produced, the rate of production was disappointing. The process would not be economic under present conditions.

1963

7.100 Reactivity of coals in high-pressure gasification with hydrogen and steam. Harlan L. Feldkirchner and Henry F. Linden (Inst. of Gas Technol., Chicago). Ind. Eng. Chem., Process Design Develop. 2, 153-62 (1963). The rates of reaction of various coals and chars with H₂, steam, and H-steam mixts. were measured at pressures up to 2500 lb./sq. in. gage and temps. up to 1700°F. A rapid-charge, semiflow reactor system was used in which very short coal heat-up and product-gas residence times were obtained. The primary variables studied were temp., C conversion, total pressure, and feed gas compn. By means of the novel exptl. technique employed, it was possible

to follow directly the course of the coal-H-steam reactions during the initial high-rate period. The information obtained is of value in the design of reactors for conversion of coal to CH₄.

7.101 Pressure gasification of bituminous coal in Dorsten. Georg Gruson. Freiberger Forschungsh. A256, 5-25 (1963). An address. The economic aspects of producing pipeline gas by using Lurgi high-pressure gasifiers appear favorable. The large-scale operation of the Dorsten (German) plant is successful. The connection of many single process steps in series favors the production of high-quality materials and influences the economic efficiency of the process. The economics of a synthetic pipeline gas plant by gasifying bituminous char in Lurgi generators was critically evaluated (cf. Katell, et al., U. S. Bur. Mines, Rept. Invest. No. 5547 (1959)).

7.102 Fixed-bed pressure-gasification pilot plant for operating under slagging conditions. Anon. Gas Coke 25, 144-7, 160 (1963). This is a report of investigations conducted at the fixed-bed gasification project at Grand Forks, North Dakota, to treat U. S. lignites. It covers a description of the pressure gasifier, slagging technique, and a comparison with the Lurgi process at Morwell.

7.103 Process and plant for distillation of coal and similar materials. Jean Makhonine. Fr. 1,367,716 (Cl. C 10b), July 24, 1964, Appl. June 14, 1963; 3 pp. In a process for simultaneous dry distn. and hydrogenation of coal, the retort consists of a vertical cylindrical furnace. The bottom of the furnace contains molten Fe or Ag, and the remaining space is filled with coal which floats on top of the molten metal. Part of the C resulting from the action of heat on the coal dissolves in the melt. Steam is blown through the melt at $\pm 1000^\circ$ and reacts rapidly with the dissolved C, giving hydrocarbons and C oxides, which, at a high temp., pass through the upper layers of coal causing partial carbonization and distn. The process is continuous, fresh charge being added to, and gaseous products (at 200°) removed from, the furnace top. High thermal efficiency and close temp. control are achieved either by elec. heating of the metal pool or by mixing air or O with the steam input. Adjustment of conditions can result in conversion of coal completely into gaseous or completely into liquid products, or into a variety of mixts. of these, with or without production of high-quality coke.

7.104 Some aspects in the design of a gasifier. M. Ramacharyulu, K. Seshagiri Rao, M. G. Krishna, and S. H. Zaheer (Regional Res. Lab., Hyderabad). Indian Chem. Engr. 5(3), 133-8 (1963). The design of an atm., slagging gasifier based on the coal and ash analysis is given.

7.105 Thermodynamic evaluation of high-pressure coal gasification. D. B. Scully (Univ. Manchester, Engl.). Chem. Eng. Sci. 18, 725-7 (1963). The concns. of CO_2 , CO , H_2O , H_2 , and CH_4 at equil. under conditions corresponding to those for coal gasification were calcd. and comparison made with data for 2 Lurgi generators. The network parameters for calcn. were $\text{H}_2\text{O}:\text{O}_2$ ratios of 3:1 and 4:1; temps. of 1000, 1200, and 1400°K.; and pressures of 1, 11, 21, and 31 atm. At 1000°K., there is a large increase in CH_4 formation in going from 1 to 31 atm.

1962

7.106

Synthesis gas production by the Koppers-Totzek process. Wilhelm Kurt Konnerth. Nitrogen 19, 30-6 (1962). Since synthesis gas is the basic material for large-scale synthesis of NH_3 , MeOH, higher alcs., liquid fuels, and kerosene, its compn. should be const. regardless of the gas production process employed. This requires independence from any particular feedstock, such as coal, oil, hydrocarbon liquids, or gases contg. hydrocarbons, and also the possibility of manufg. the synthesis gas in one phase. The gas must be free of condensable hydrocarbons and gum-formers, and it should have a low content of CH_4 and org. S compds. The process must operate well even at a high gasification efficiency. Neither low-temp. tar nor phenolic waste waters should be produced. Developments in the gasification of coal from 1831 to 1938 are mentioned briefly. The historical development of the K-T process since 1938 includes the statement that the 24-ton/day large-scale pilot plant of the U. S. Bureau of Mines in Louisiana, Mo., confirmed the results obtained on a Ruhr pilot plant before its destruction in 1943. General operational procedures are shown for the gasification of coal dust and for the gasification of oil. From 1949 to 1961, 8 plants with a total capacity of 75,000 cu.m./hr. CO plus H were built abroad by H. Koppers G.m.b.H. Operating results for plants in Finland, Japan, Spain, and Belgium include: the analysis and consumption of coal feed and oil feed, the consumption of steam and O , the analysis and production of raw gas, and the production of steam in a waste heat boiler. Neither operating nor production costs are included.

7.107 Pressure gasification of solid fuels. Wolfgang Roth. Freiberger Forschungsh. A289, 91-127 (1962). The history of the Lurgi fixed-bed gasifier is reviewed and recent developments are described to increase the capacity of the gasifier and improve the economy of the process. 48 references.

7.108 Coal gasification in Great Britain. F. J. Dent, T. S. Ricketts, and M. Maccormac. World Power Conf., 6th, Melbourne, paper No. 140-11-3/6 (1962). The installation of 2

Lurgi plants of medium size is the major com. advance in coal gasification results for 6 months' operation are given for one in Scotland. Research activities have concerned methods of enrichment, pressure gasification with enriched air in place of O_2 , and the development of a slagging pressure gasifier. The methods of enrichment include use of CH_4 and liquefied petroleum gas, hydrogenation of various types of oil, and catalytic gasification of light distillate. Among the atm.-pressure gasifiers are the double-shaft Otto-Rummel plant and the Ruhrgas cyclone.

7.109 Gasification of bituminous coal with oxygen in a pilot plant equipped for slurry feeding. L. F. Wilmott, K. D. Plants, W. R. Huff, and J. H. Holden (U. S. Bur. of Mines, Morgantown, W. Va.). U. S. Bur. of Mines, Rept. Invest. No. 6117, 10 pp. (1962). Pulverized high-volatile A bituminous coal was gasified with O_2 and superheated steam in a pressure-gasification pilot plant. The min. ratio of H_2O to pulverized coal that could be pumped as a slurry was about 1:1. Heating this slurry produced a suspension of coal in superheated steam having a steam:coal ratio greater than the 0.3:1 proportion that is considered optimum for pressure gasification of pulverized coal. A steam separator removed enough steam to provide ratios down to about 0.5:1, but a 0.3:1 ratio was not achieved. Gasification of Sewickley coal produced a synthesis gas contg. H_2 36, CO 46, and CO_2 13%. Gas output, gas compn., and coal and O_2 requirements were the same as for a pilot plant equipped for fluidized-coal feeding. Typical results from the slurry-fed plant at 300 lb./sq. in. gage were C gasified 95%, coal requirements 34 lb./1000 cu. ft. of $CO + H_2$ produced, and O_2 requirements 365 cu.ft./1000 cu. ft. $CO + H_2$. The 2 feeding methods are equally satisfactory from the standpoint of gasification.

7.110 Make high-BTU pipeline gas from coal. Harry Perry (U. S. Bur. of Mines, Washington, D.C.). Hydrocarbon Process. Petrol. Refiner 41, No. 7, 89-94 (1962). Exptl. and demonstration work on conversion of coal to synthesis gas and subsequently to high-BTU gas is described. Entrained, fluidized, and fixed-bed processes are discussed and compared with 2-stage process, a slag-bath generator, and a nuclear-heat reactor. Expts. in underground gasification of coal are described, the results indicating that this process is workable but uneconomic. Methanation of synthesis gas and direct hydrogasification of coal are compared. Work is continuing in the fields of pressure gasification, catalyst improvement, and gas purification. It is concluded that processes are available for producing economic pipeline gas from coal when required.

1961

7.111 Coal gasification for production of synthesis and pipeline gas. Martin A. Elliott (Inst. of Gas Technol., Chicago). Trans. AIME 220, 134-51 (1961). The use of O, the development of suspension gasification processes and fluidized-bed gasifiers, and the operation of gasifiers under slagging conditions are discussed. 110 references.

7.112 Combustion of coal by gasification. Kensuke Kawashimo and Kozo Katayama (Tokyo Inst. Technol.). Bull. JSME 4, 422 (1961). A new type of continuous pilot-scale gas producer was stoked with bituminous coal (19.37% ash). At a gasification rate of 300 kg./sq. m. hr., the hot efficiency was 93.9%. Operation of another exptl. producer showed the feasibility of gasifying coal contg. 43.13-61.5% ash.

7.113 Hydrogen from hydrocarbon gas and steam. Everett Gorin (to Consolidation Coal Co.). U.S. 3,188,179 (Cl. 23-212), June 8, 1965, Appl. April 10, 1961; 6 pp. Coal is extd. with solvent to produce an ext. and residue. The ext. is sepd. and the residue is carbonized to produce distillate tar and char. The tar is hydrocracked in the presence of H to produce an off-gas and a liquid product. The off-gas is converted to H and the CO₂ acceptor is calcined; the heat for calcination is supplied by burning the carbonization char. H is produced at 660-872°, 73-295 psi., an upward gas velocity of 0.5-3.0 ft./sec. of steam and off-gas, and 2-5 moles steam per mole C in off-gas in the presence of a fixed-bed, steam-reforming catalyst and fluidizable CO₂-acceptor particles. Cf. CA 56, 13176g; 60, 2565b.

7.114 Pressure gasification of solid fuels with oxygen in Germany. Hellmuth Weittenhiller. Inst. Gas. Engrs., Publ. 1, 655-69 (1961); cf. CA 56, 7618c. Practical operation of a coal gasification plant with O under pressure, installed in 1955 at Dorsten (Westphalia), is described. New developments, considering mainly redn. in temp., corrosion problems due to Cl, detoxification of the crude gas, and O-enriched air, have considerably improved the yields and economics of the process.

7.115 Pressure gasification with oxygen of solid fuels in Germany. Hellmuth Weittenhiller (Steinkohlgas A.-G., Dorsten, W. Ger.). Gas Times 95, No. 959, 25-6 (1961). The process changes needed to use bituminous coal in Lurgi brown-coal gasifiers are described. The most important is to lower the temp. of the high-pressure steam. Improvements in the gasification process are also made by converting CO by using the steam content of the crude gas and by replacement of pure O with enriched air.

7.116 Producer gas warrants new attention. G. W. Hamilton. Coal Utilization 15 (16), 2 pp. (1961). Past history, current status, and details of a new gas producer are discussed. The Wellman-Galusha gas producer on coke or anthracite has an overall gasification efficiency of about 90%. If the gas must be washed, a portion of the sensible heat, roughly 5%, is lost when the temperature of the gas is brought down from ~600°F to the temp. of the wash water. From Gas Abstr. 18 (2), 41 (1962).

7.117 Gasification of Chernomore coals in gas generators. Ts. Tsenkov. Godishnik Nauchnoizsled. Inst. Goriva Toplotekhn. (Sofia) 6, 89-102 (1960). Results are given of plant expts. on intensification of gasification of Chernomore coals in a Koeller-type gas generator having an internal diam. of 2.6 m. and a rotating grate. The gasified coal contained 18-19% volatile matter and had high ash (30-4%) and S (3.5%) contents. The slack content was >35%. Expts. were made at 165, 272, and 336 kg./sq. m./hr. rate of charging. A further increase in charging rate was limited by the capacity of the blowing app. The max. rate of charging was the most efficient. At 336 kg./sq. m./hr., 2602 cu. m./hr. of gas was produced. The gas had the following compn.: CO₂ 6.19, H₂S 1.50, C_nH_m 0.49, O₂ 0.60, CO 24.94, H₂ 18.85, CH₄ 4.01, and N₂ 43.42 vol. %. The yield of gas was 2.72 cu.m./kg. of coal. The height of the coal layer in the gas generators was 1.3-1.7 m., the consumption of air 1420 cu.m./hr., and the H₂O-vapor content 90.8 g./cu. m. The heat of the discharged slag can be used most efficiently for evapn. of H₂O.

7.118 Coal gasification--Sumitomo process. Toshio Taniyama and Yoshiichi Karato. Chem. Eng. Progr. 56, No. 8, 66-70 (1960). The method developed by the Sumitomo Chem. Co. (Japan) is a normal-pressure gasification in which a mixt. of pulverized coal, O, and steam is jetted diagonally downward into the gasifier from the lower part of the vertical, cylindrical furnace and from which slag is sepd. by an upward vortex current, collected at the bottom of the furnace, and discharged at a comparatively low temp. A pilot-plant scale unit was completed and a 50-ton coal/day unit operated continuously for 3000 hrs. in 1956.

7.119 Intensifying the gasification process under pressure. M. I. Rabinovich. Akad. Nauk Ukr. R.S.R., Inst. Teplo-energet., Zbirnik Prats 1960, No. 19, 20-32 (Russian summary). Factors affecting the productivity of gas generators under pressure are discussed and the possibility of increasing gas production to 3000 cu.m./sq. m./hr. at 20-25 atm. is outlined on the basis of data obtained from the gasification of Irsha-

Borodin brown coal at 5 and 10 atm. Coals with high ash content are less suitable for gas production.

1959

7.120 Improving the thermal efficiency and operation of a gas producer. Office Central de Chauffage Rationnelle. Brit. 922,892, Apr. 3, 1963; Fr. Appl. Apr. 30 and Nov. 30, 1959; 6 pp. Producer gas, made by gasifying a liquid or solid fuel in air, is passed countercurrently to a stream of inert material which removes the sensible heat and the suspended carbon black from the gas. The material on the inert solids is gasified with air and steam to make addnl. gas. The thermal efficiency of the gasifier is improved 20-5%.

1958

7.121 Production of high-caloric gases in Lurgi-system furnaces by low-temperature carbonization of lignite. H. G. Riedl (Otto Grotewohl Kombinat, Boehlen, E. Ger.). Paliwa 38, 375-8 (1958). Plant experiences are described of the gasification of East German lignite briquets at 610-50°. The temp. had to be raised to 710° only occasionally. Between 850 and 950 cu. m. of air was used per long ton of coal. Typical analyses of the raw gases are: CO₂ 16.0-22.0, H₂S 2.5-3.5, C_nH_m 0.5-1.5, O₂ 0.1-0.2, CO 16.0-26.0, H 23.0-8.0, CH₄ 18.0-21.0, N 8.0-12.0 % by vol.

1957

7.122 Gasification properties of Dimitrovsk coals. Ts. G. Tsenkov. Godishnik Nauchnoizsled. Inst. Goriva Toplotekhn. (Sofia) 7, No. 2, 45-70 (1961). Results of a study on gasification of Dimitrovsk brown coals are discussed. The study was made by the Mikheev method (Gazifikatsiya Tverdogo Topliva, Gostoptekhnizdat, Moskva, 1957, pp. 21-32) in a lab. app. simulating gasification in a stationary coal layer. Simultaneously, the app. registers slag formation of coal, its reaction with O from the air, and its thermal stability. Samples of coal contg. various amts. of ash were taken from various coal beds and mines. The fact that gasification of coal varies with mineral content was ascertained. An increased amt. of ash results in lowering activity indexes toward O in the air and in worsening of slag formation. Coals from various beds and mines having the same ash content have similar gasification properties.